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1905.

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BUNGAY, SUFFOLK.

REPORT OF

THE INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS.

THE Council has ordered the following letter and report to be printed in the Journal and Proceedings of the Society:

GOVERNMENT LABORATORY,
CLEMENT'S INN PASSAGE,
STRAND, LONDON, W.C.
10*th November*, 1905.

GENTLEMEN,

I have the honour to transmit to you the Report of the International Committee on Atomic Weights, 1906, to which I have appended the signatures of Professors Moissan and Seubert as desired by them.

It will be seen that the Committee, for the reasons stated in the Report, are not prepared to advise any immediate alteration in the values for the atomic weights given in their last Report. They recommend, however, in conformity with the desires of the great majority of the Larger Committee, that the values in the table for 1906 be given on the basis of $O = 16$, to the exclusion of those on the basis of $H = 1$.

I am, Gentlemen,

Your obedient Servant,

T. E. THORPE.

The Hon. Secretaries,
The Chemical Society,
Burlington House,
London, W.

Report of the International Committee on Atomic Weights.

During the year 1905 there has been unusual activity in the determination of atomic weights, and some of the work done relates to the most fundamental values. The entire system of atomic

weights is thus affected more or less profoundly, and a general revision of the table would seem to be needed within the near future. Neglecting minor investigations, the more important determinations published since our last report are briefly as follows :

Cadmium.—Atomic weight determined by Baxter and Hines (*J. Amer. Chem. Soc.*, 1905, **27**, 222), by analysis of the chloride. Three measurements of the ratio $CdCl_2 : 2AgCl$ gave in mean $Cd = 112{\cdot}476$. Six measurements of the ratio $CdCl_2 : 2Ag$ gave in mean $Cd = 112{\cdot}462$. General mean of both series, 112·469 ; when $Ag = 107{\cdot}93$ and $Cl = 35{\cdot}473$. As additional determinations are promised, based upon a study of cadmium bromide, a change in the atomic weight of cadmium as given in our table may properly be deferred.

Carbon.—From the ratios published in 1904, relative to the basic acetate and acetylacetonate of glucinum, Parsons (*J. Amer. Chem. Soc.*, 1905, **27**, 1204 ; *Zeit. anorg. Chem.*, 1905, **46**, 215) has computed the atomic weight of carbon. The values obtained by treating the two ratios algebraically are $Gl = 9{\cdot}112$ and $C = 12{\cdot}007$. As the latter figure is quite independent of all previous determinations it has distinct corroborative significance.

Chlorine and Sodium.—In a very elaborate investigation upon the atomic weights of chlorine and sodium, Richards and Wells * have shown that the data furnished by Stas are affected by appreciable errors. Ten syntheses of silver chloride gave, in mean, $Cl = 35{\cdot}473$ when $Ag = 107{\cdot}93$. From ten measurements of the ratio $Ag : NaCl$, and ten of the ratio $AgCl : NaCl$, with the foregoing values for silver and chlorine, $Na = 23{\cdot}008$. Stas's values are $Cl = 35{\cdot}455$ and $Na = 23{\cdot}048$.

The results just cited are obviously indirect, for they depend upon the atomic weight of silver. The experiments published by Dixon and Edgar † are therefore of peculiar interest, for they involve the intervention of no intermediate quantities between the atomic weights of chlorine and hydrogen. Hydrochloric acid was directly synthesised from weighed amounts of hydrogen and chlorine, and nine concordant determinations gave, in mean, $Cl = 35{\cdot}195, \pm 0{\cdot}0019$, referred to the hydrogen standard. With $O = 16$, Cl becomes 35·463, a value nearly midway between that found by Stas and the new figure given by Richards and Wells. Considering the difficulties of the work, the agreement between this and the previous investigations is as close as could be reasonably expected.

Gadolinium.—Urbain (*Compt. rend.*, 1905, **140**, 583), from ten

* Published by the Carnegie Institution of Washington, 70 pp., April, 1905. See also *J. Amer. Chem. Soc.*, 1905, **27**, 459.

† *Chem. News*, 1905, **91**, 263. Memoir read before the Royal Society.

analyses of the octohydrated sulphate, finds Gd = 157·23; when H = 1·007 and S = 32·06. This value is more than a unit higher than that given in the table, and is probably more trustworthy.*

Iodine.—Baxter has continued his research of 1904 upon the atomic weight of iodine, and has published a second memoir upon this subject (*J. Amer. Chem. Soc.*, 1905, **27**, 876). First, from eight conversions of silver iodide into bromide, by heating in bromine, he found I = 126·985. Two series of measurements, of five experiments in each, of the ratio AgI to AgCl, gave respectively 126·982 and 126·984. Eight determinations of the direct ratio between silver and iodine, weighed separately, gave in mean 126·987. Five determinations of the ratio I : AgI gave 126·983, and four of the ratio Ag : AgI gave 126·989. The average of all six series is I = 126·985; when Ag = 107·93, Cl = 35·473, and Br = 79·955. The last of these antecedent values was checked by a direct comparison of AgBr with AgCl, and the mean of six experiments gave Br = 79·953. The value previously found by Baxter was 126·975 for iodine, and the difference is partly due to his use, in the later investigation, of the new figure obtained for chlorine by Richards and Wells. The iodine work, therefore, is confirmatory of the latter.

Nitrogen.—R. W. Gray, in a preliminary notice (*Proc.*, 1905, **21**, 156), gives the results of his experiments upon nitric oxide. Ten determinations of the density of the gas, corrected by D. Berthelot's formula, give a molecular weight of 30·005, whence N = 14·005. Six analyses of nitric oxide, effected by burning finely-divided nickel in it, gave N = 14·006. The investigation was to be continued farther.

Guye, in an interesting lecture before the Chemical Society of Paris,† has given a complete summary of the researches relative to this atomic weight, which have been conducted by him and his associates at Geneva. He also discusses, somewhat fully, all previous determinations of the constant, and concludes, mainly from the physical evidence, that the atomic weight of nitrogen is not far from 14·01, and that the value 14·04, obtained by Stas, is no longer tenable. Going still farther, he reverses the ordinary gravimetric ratios from which the accepted atomic weight of nitrogen was derived, and, applying to them the new value for N, he deduces the atomic weight of silver. The latter is thus reduced from 107·93 to below 107·89, ranging even as low as 107·871. For these low values Guye cites much confirmatory evidence, which is not to be lightly disregarded. To this point we shall recur later.

* See Eberhard, *Zeit. anorg. Chem.*, 1905, **45**, 374; on the spectroscopic purity of the rare earth oxides studied by Urbain and others.

† *Bull. Soc. Chim.*, Aug. 5, 1905, with independent pagination. Compare Richards, *Proc. Amer. Phil. Soc.*, 1904, **43**, 116.

Potassium.—Atomic weight redetermined by Archibald (*Trans. Roy. Soc. Canada,* Series 2, **10**, section iii, p. 47) through analysis of the chloride. Four measurements of the ratio AgCl : KCl gave K = 39·139, and four of the ratio Ag : KCl gave 39·140; when Ag = 107·93 and Cl = 35·455. If Cl = 35·473, then K becomes 39·122.

Silicon.—W. Becker and J. Meyer (*Zeit. anorg. Chem.*, 1905, **43**, 251; **46**, 45) have determined the atomic weight of silicon by conversion of the chloride into the oxide. Eight determinations were made, and, in sum, 46·82400 grams of $SiCl_4$ gave 16·58236 grams of SiO_2. Hence, with Cl = 35·45, Si = 28·207. With the Richards-Wells value for chlorine, 35·473, Si becomes 28·257. Additional determinations by a different method are promised. This paper is preceded by an essay by Meyer on the calculation of atomic weights (*ibid.*, p. 242), which deserves careful consideration.

Strontium.—From four measurements of the ratio 2Ag : $SrCl_2$, Richards (*Proc. Amer. Acad.*, 1905, **40**, 603) finds Sr = 87·661, when Ag = 107·93 and Cl = 35·473. This confirms the earlier value derived by Richards from experiments upon strontium bromide.

Tellurium.—Gallo (*Atti Accad. Lincei*, 1905, [v], **14**, 23 and 104) has determined electrolytically the ratio between silver and tellurium. From twelve experiments, in mean, Te = 127·61, when Ag = 107·93. Incidentally to this work, as a check upon the method employed, four comparisons between silver and copper were made. In mean, Cu = 63·58.

Thorium.—R. J. Meyer and Gumperz (*Ber.*, 1905, **38**, 817) have attempted to separate ordinary thorium into fractions of different atomic weight, and have failed to verify the observations of Baskerville. The fractions obtained by various processes gave atomic weights varying from 232·2 to 232·7, values which are essentially identical with that given in the table.

From the foregoing summary of results, it becomes evident that a far-reaching series of changes will soon be needed in our system of atomic weights. A change in chlorine or nitrogen implies many other changes in the table, and if the accepted value for silver should be modified the alterations would be most sweeping. The atomic weights of silver, chlorine, and bromine enter into the calculation of nearly all other atomic weights, and form, so to speak, the platform upon which the entire structure stands.

The changes, however, which are suggested at present, are not final. Work is in progress in several laboratories which may confirm or modify many of the accepted values, and until that work is finished, at least so far as the fundamental data are concerned, it is wisest for us to suspend judgment and await developments. Were we to reconstruct the table of atomic weights on the basis of the evidence now

before us, we should do it imperfectly, and a new revision would be demanded next year or the year after. Confusion would inevitably follow. Fortunately, the matter is not urgent, for the corrections which now seem desirable are not large, and the existing figures are accurate enough for all ordinary purposes. We therefore recommend that the table for 1905 be continued in use without change during 1906, even although some modifications are theoretically desirable. A year hence we shall be in a better position for a critical adjustment of the data, and no harm can follow from the delay. In accordance with the expressed wish of a majority of the larger committee, we also recommend that the table based upon the oxygen standard be made official. So far as this committee is concerned, the private opinions of its members will be subordinated to the desires of the majority, and the table referred to hydrogen will no longer appear as a part of its report.

For the present, a few suggestions may not be unacceptable, which follow from an examination of the lecture by Guye. Rayleigh, Leduc, Guye, Gray, and others, from their studies of nitrogen and its oxides, have accumulated a mass of strong evidence in favour of a lower value for nitrogen. The data furnished by Stas, on the other hand, point to the higher value which has heretofore been generally adopted. Can we abandon the one in favour of the other, and accept the new figure without reserve?

On behalf of the new figure for nitrogen, we must admit that the determinations are remarkably concordant, and that they rest upon a direct comparison of the element with oxygen. The Stas values, with their confirmations by other chemists, are also very concordant, but they are indirect. They all rest primarily upon the atomic weights of silver, chlorine, and bromine, and these were connected with oxygen through experiments upon chlorates and bromates. Our whole system of atomic weights, with only a few exceptions, is based to-day upon the analyses of several oxyhalogen salts. Their accuracy is assumed, and all anomalies which appear in determinations based upon other lines of research are commonly ascribed to undiscovered errors. The assumption may be sustained, but it is not yet beyond the reach of criticism.

Consider, for example, the well-known ratio $Ag : AgNO_3 = 100 : 157{\cdot}149$. If $Ag = 107{\cdot}93$, as determined through the analyses of chlorates and bromates, then $N = 14{\cdot}037$, or $14{\cdot}04$ as given in our table. If, on the other hand, $N = 14{\cdot}009$, as given by Guye, Ag becomes $107{\cdot}881$. The difference between the two values for silver evidently represents a difference in our methods of connecting the element with oxygen, the latter being taken as the standard. For each method strong arguments are possible, and for each value other

corroborative testimony can be cited. Neither procedure is wholly free from objections, and the final conclusion, therefore, is one of uncertainty. We cannot safely reject either line of evidence, nor can we accept one as surely more exact than the other. Concordant values for silver can be derived from either method of discussion, as Guye has shown, and through them the entire system of atomic weights is affected.

In this condition of affairs, the position of the committee can only be one of conservatism. It is better to retain the table we have until at least some of the doubts which now affect it have been eliminated. It seems to be essential that the foundations of the atomic weight table should be both broadened and strengthened, and that new lines of research connecting the fundamental values with oxygen shall be investigated. Some work of this kind is already promised from the laboratory of Harvard University, to be carried out by Richards and his colleagues, but that need not exclude other activities. It is to be hoped that a number of investigators may take up the consideration of this problem, and that the methods of attack upon it may be multiplied. The careful study of such salts as the sulphates, carbonates, and nitrates might perhaps be profitable. Whether the organic salts of silver could be utilised for good atomic weight determinations is still uncertain.

F. W. Clarke.
Henri Moissan.
Karl Seubert.
T. E. Thorpe.

1906.

International Atomic Weights.

		O=16.			O=16.
Aluminium	Al	27·1	Neodymium	Nd	143·6
Antimony	Sb	120·2	Neon	Ne	20
Argon	A	39·9	Nickel	Ni	58·7
Arsenic	As	75·0	Nitrogen	N	14·04
Barium	Ba	137·4	Osmium	Os	191
Bismuth	Bi	208·5	Oxygen	O	16·00
Boron	B	11	Palladium	Pd	106·5
Bromine	Br	79·96	Phosphorus	P	31·0
Cadmium	Cd	112·4	Platinum	Pt	194·8
Cæsium	Cs	132·9	Potassium	K	39·15
Calcium	Ca	40·1	Praseodymium	Pr	140·5
Carbon	C	12·00	Radium	Rd	225
Cerium	Ce	140·25	Rhodium	Rh	103·0
Chlorine	Cl	35·45	Rubidium	Rb	85·5
Chromium	Cr	52·1	Ruthenium	Ru	101·7
Cobalt	Co	59·0	Samarium	Sm	150·3
Columbium	Cb	94	Scandium	Sc	44·1
Copper	Cu	63·6	Selenium	Se	79·2
Erbium	Er	166	Silicon	Si	28·4
Fluorine	F	19	Silver	Ag	107·93
Gadolinium	Gd	156	Sodium	Na	23·05
Gallium	Ga	70	Strontium	Sr	87·6
Germanium	Ge	72·5	Sulphur	S	32·06
Glucinum	Gl	9·1	Tantalum	Ta	183
Gold	Au	197·2	Tellurium	Te	127·6
Helium	He	4	Terbium	Tb	160
Hydrogen	H	1·008	Thallium	Tl	204·1
Indium	In	115	Thorium	Th	232·5
Iodine	I	126·97	Thulium	Tm	171
Iridium	Ir	193·0	Tin	Sn	119·0
Iron	Fe	55·9	Titanium	Ti	48·1
Krypton	Kr	81·8	Tungsten	W	184
Lanthanum	La	138·9	Uranium	U	238·5
Lead	Pb	206·9	Vanadium	V	51·2
Lithium	Li	7·03	Xenon	Xe	128
Magnesium	Mg	24·36	Ytterbium	Yb	173·0
Manganese	Mn	55·0	Yttrium	Yt	89·0
Mercury	Hg	200·0	Zinc	Zn	65·4
Molybdenum	Mo	96·0	Zirconium	Zr	90·6

INSTRUCTIONS TO ABSTRACTORS,

GIVING THE

NOMENCLATURE AND SYSTEM OF NOTATION

ADOPTED IN THE ABSTRACTS.

The object of the abstracts of chemical papers published elsewhere than in the Transactions of the Society is to furnish the Fellows with a concise account of the progress of chemical science from month to month. It must be understood that as the abstracts are prepared for the information of the Fellows in general, they cannot possibly be made so full or so detailed as to obviate on the part of those who are engaged on special investigations the necessity of consulting the original memoirs.

1. Titles of papers must be given literally.
2. Before beginning to write the abstract, the whole of the original paper must be read, in order that a judgment may be formed of its importance and of the scale on which the abstract should be made.
3. In the case of papers dealing with subjects not strictly chemical, the abstract should refer only to matters of chemical interest in the original.
4. The abstract should consist mainly of the expression, in the abstractor's own words, of the substance of the paper.
5. The abstract should be made as short as is consistent with a clear and accurate statement of the author's results.
6. If an abstract of a paper on the same subject, either by the author of the paper abstracted, or by some other author, has already appeared, note should, as a rule, be made of this fact.
7. Matter which has appeared once in the *Abstracts* is not to be abstracted again, a reference being given to the volume in which the abstract may be found.
8. As a rule, details of methods of preparation or analysis, or generally speaking of work, are to be omitted, unless such details are essential to the understanding of the results, or have some independent value. Further, comparatively unimportant compounds, such as the inorganic salts of organic bases or acids, should be mentioned quite shortly. On the other hand, data such as melting and boiling points, sp. gr., specific rotation, &c., must be given in every case unless recorded in earlier papers.

Nomenclature.

9. Employ names such as *sodium chloride, potassium sulphate* for inorganic compounds, and use the terminals *ous* and *ic* only in distinguishing compounds of different orders derived from the same elementary radicle; such, for instance, as mercurous and mercuric chlorides, sulphurous and sulphuric acids.

10. Term compounds of metallic radicles with the OH-group *hydroxides* and not hydrates, the name hydrate being reserved for compounds supposed to contain water of combination or crystallisation.

11. Term salts containing an amount of metal equivalent to the displaceable hydrogen of the acid, *normal* and not neutral salts, and assign names such as sodium hydrogen sulphate, disodium hydrogen phosphate, &c., to the acid salts. Basic salts as a rule are best designated merely by their *formulæ*.

12. Names in common use for oxides should be employed, for example: NO, nitric oxide; CO_2, carbon dioxide; P_4O_{10}, phosphoric oxide; As_4O_6, arsenious oxide; Fe_2O_3, ferric oxide.

13. In open chain compounds, Greek letters must be used to indicate the position of a substituent, the letter α being assigned to the first carbon atom in the formula, except in the case of CN and CO_2H, for example, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2I$ α-iodobutane, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CN$ α-cyanopropane.

14. Isomeric open chain compounds are most conveniently represented as substitution derivatives of the longest carbon chain in the formula; for example,

$$\begin{matrix}CH_3\\CH_3{\cdot}CH_2\end{matrix}\!\!>\!CH{\cdot}CH\!<\!\!\begin{matrix}CH_3\\CH_3\end{matrix} \text{ or } CH_3{\cdot}CH_2{\cdot}CHMe{\cdot}CHMe{\cdot}CH_3$$

should be termed $\beta\gamma$-dimethylpentane, not methylethyl*iso*propylmethane, and $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH{\cdot}CH\!<\!\!\begin{matrix}CH_3\\CO_2H\end{matrix}$ or $CH_3{\cdot}CHMe{\cdot}CHMe{\cdot}CO_2H$ should be termed $\alpha\beta$-dimethylbutyric acid, not $\alpha\beta\beta$-trimethylpropionic, or α-methyl*iso*valeric, or methyl*iso*propylacetic acid.

15. Use names such as methane, ethane, &c., for the normal paraffins or hydrocarbons of the C_nH_{2n+2} series of the form $CH_3{\cdot}[CH_2]_5{\cdot}CH_3$, &c. Term the hydrocarbons C_2H_4 and C_2H_2 ethylene and acetylene respectively (not ethene and ethine). Homologues of the ethylene series are to be indicated by the suffix *-ene*, and those of the acetylene series, wherever possible, by *-inene*. Adopt the name allene for the hydrocarbon $CH_2{:}C{:}CH_2$.

16. Distinguish all hydroxyl derivatives of hydrocarbons by names ending in *ol*. Alcohols should be spoken of as mono-, di-, tri-, or n-hydric, according to the number of OH-groups. Compounds which are not alcohols, but for which names ending in *ol* have been used, are to be represented by names ending in *ole*, if a systematic name cannot be given, thus anisole not anisol, indole not indol. Compounds such as MeONa, EtONa, &c., should be termed sodium methoxide, sodium ethoxide, &c.

17. The radicles indicated in the name of a compound are to be

given in the order fluoro-, chloro-, bromo-, iodo-, nitro-, nitroso-, amino-, imino-, cyano-, thiocyano-, hydroxy-, keto-.

18. Compounds analogous to the acids of the lactic series containing the OH-group should be termed *hydroxy*-derivatives, and not oxy-derivatives; for example, hydroxyacetic and not oxyacetic acid. Compounds containing the analogous groups OEt, OPh, OAc, &c., should in like manner be termed ethoxy-, phenoxy-, acetoxy- derivatives. Thus α-ethoxypropionic acid, $OEt \cdot CHMe \cdot CO_2H$, instead of ethyl-lactic acid; 3:4-diethoxybenzoic acid, $(OEt)_2C_6H_3 \cdot CO_2H$, instead of diethylprotocatechuic acid; and α-acetoxypropionic acid, $OAc \cdot CHMe \cdot CO_2H$, instead of acetyl-lactic acid. Terms such as diethylprotocatechuic acid should be understood to mean a compound formed by the displacement of hydrogen atoms in the hydrocarbon radicle of protocatechuic acid by ethyl, thus, $C_6HEt_2(OH)_2 \cdot CO_2H$, and not $C_6H_3(OEt)_2 \cdot CO_2H$, just as dibromoprotocatechuic acid is understood to be the name of a compound of the formula $C_6HBr_2(OH)_2 \cdot CO_2H$.

19. The term *ether* should be restricted to the oxides of hydrocarbon radicles and their derivatives, and the esters (so-called compound ethers or ethereal salts) should be represented by names similar to those given to metallic salts.

20. When a substituent is one of the groups NH_2, NHR, NR_2, NH or NR, its name should end in *ino*; for example, β-aminopropionic acid, $NH_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$, β-anilino-acrylic acid, $NHPh \cdot CH \vdots CH \cdot CO_2H$, α-iminopropionic acid, $NH \vdots CMe \cdot CO_2H$.

21. Compounds of the radicle SO_3H should, whenever possible, be termed sulphonic acids, or failing this, sulpho-compounds; for example, benzenesulphonic acid, sulphobenzoic acid.

22. Basic substances should invariably be indicated by names ending in *ine*, as aniline instead of anilin, the termination *in* being restricted to certain neutral compounds, viz., glycerides, glucosides, bitter principles, and proteids, such as palmitin, amygdalin, albumin. The compounds of basic substances with hydrogen chloride, bromide or iodide should always receive names ending in *ide* and not *ate*, as morphine hydrochloride and not morphine hydrochlorate.

23. The Collective Index, 3rd decade (1893–1902) should be adopted as the standard of reference on questions of nomenclature not provided for in the preceding sections.

Notation.

24. In empirical formulæ the elements are to be given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

25. Equations should be omitted unless essential to the understanding of the results; as a rule, they should not be written on a separate line, but should "run on" with the text.

26. To economise space, it is desirable:

(a) That *dots* should be used instead of *dashes* in connecting contiguous symbols or radicles, whenever this does not interfere with the clearness of the formula.

(b) That formulæ should be shortened by the judicious employment of the symbols Me for CH_3, Et for C_2H_5, Pr^{α} for $CH_2{\cdot}CH_2{\cdot}CH_3$, Pr^{β} for $CH(CH_3)_2$, Ph for C_6H_5, Py for C_5H_4N, Ac for $CO{\cdot}CH_3$, and Bz for $CO{\cdot}C_6H_5$.

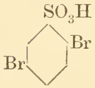
(c) That formulæ should be written *in one line* whenever this can be done without obscuring their meaning.

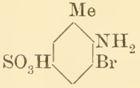
27. In representing the constitution of benzene derivatives, the relative positions of the radicles in the symbol of benzene should be indicated by numerals, instead of by means of the hexagon formula.

(a) The abbreviations *o*-, *m*-, and *p*-, should be used in place of 1 : 2- or ortho-, 1 : 3- or meta-, and 1 : 4- or para.

(b) In numbering positions in the case of substitution derivatives of phenol, aniline, benzonitrile, benzoic acid, benzenesulphonic acid, benzaldehyde, and toluene, the characteristic radicle of each of these parent substances is to be regarded as in position 1 (compare Collective Index).

(c) Names of substitution derivatives should be given in such a way that the position of the substituent is indicated by a numeral prefixed; for example :—

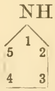

is 2 : 5-dibromobenzenesulphonic acid;

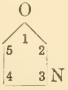

is 3-bromo-*o*-toluidine-5-sulphonic acid.

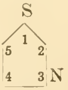
28. In representing the constitution of derivatives of other "closed chain" hydrocarbons, graphic formulæ should not be employed, but the system of numbering positions indicated in Richter's *Lexikon der Kohlenstoff-Verbindungen* (2nd edition, 1899, pp. 16—26) should be used, of which the following schemes may be regarded as typical :—


Furan.

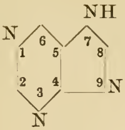

Thiophen.


Pyrrole.


Oxazole.

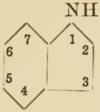

Thiazole.


Pyrazole.

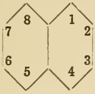


Purine.*

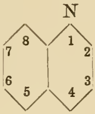
Pyridine.



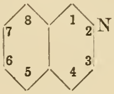
Indole.



Naphthalene.

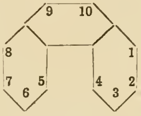


Quinoline.

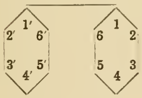


*iso*Quinoline.

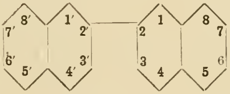
Anthracene.



Phenanthrene.



Diphenyl.



ββ-Dinaphthyl.

Manuscript.

29. In view of the difficulty of dealing with MSS. of widely varying sizes, abstracts cannot be accepted unless written on quarto paper (10 × 8 in.).

30. Not more than one abstract must appear on a sheet.

31. When an abstract exceeds a sheet in length, the sheets must be fastened together by means of gum at the top left-hand corner.

32. The name of the abstractor must be written diagonally at the top left-hand corner of the first sheet of the abstract.

Proofs.

33. Abstractors are expected to read and correct proofs carefully, and to check all formulæ and figures against MSS.

34. All proofs, however small, must be returned to the Sub-Editor not later than 24 hours after receipt from the printers.

***** The Editor's decision, in all matters connected with the Abstracts, must be considered final.**

* This numbering, proposed originally by E. Fischer, is adopted in the text of the *Lexikon*.

JOURNALS FROM WHICH ABSTRACTS ARE MADE.

All references to Journals should give the abbreviated title, the year of publication, the series, the volume and the page; thus *Ber.* 1901, **34**, 2455; *Bull. Soc. chim.* 1901, [iii], **25**, 794; *Gazzetta* 1901, **31**, i, 554.

Abbreviated Title.	Journal.
Amer. Chem. J.	American Chemical Journal.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Physiol.	American Journal of Physiology.
Amer. J. Sci.	American Journal of Science.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Physik	Annalen der Physik.
Ann. agron.	Annales agronomiques.
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Ann. Inst. Pasteur	Annales de l'Institut Pasteur.
Ann. sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy.
Arch. Hygiene	Archiv für Hygiene.
Arch. Néerland.	Archives Néerlandaises des sciences exactes et naturelles.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Sci. phys. nat.	Archives des Sciences physiques et naturelles.
Arkiv Kem. Min. Geol.	Arkiv för Kemi, Mineralogi och Geologi.
Atti R. Accad. Sci. Torino.	Atti della Reale Accademia delle Scienze di Torino.
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Beitr. chem. Physiol. Path.	Beiträge für chemische Physiologie und Pathologie.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
* *Bied. Centr.*	Biedermann's Centralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
Bihang K. Svenska Vet.-Akad. Handl.	Bihang till Kongl. Svenska Vetenskaps-Akademiens Handlingar.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Cracow	Bulletin international de l'Académie des Sciences de Cracovie.
Bull. Coll. Agr. Tōkyō	Bulletin of the College of Agriculture, Imperial University, Tōkyō.
Bull. Geol. Soc. Amer.	Bulletin of the Geological Society of America.
Bull. Soc. chim.	Bulletin de la Société chimique de Paris.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Bull. Soc. ind. Mulhouse	Bulletin de la Société industrielle de Mulhouse.
Centr. Bakt. Par.	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Centr. Min.	Centralblatt für Mineralogie, Geologie und Palaeontologie.
* *Chem. Centr.*	Chemisches Centralblatt.

* Abstracts from the *Centralblatt* are made only in the case of papers published in journals other than those included in this list.

JOURNALS FROM WHICH ABSTRACTS ARE MADE.

Abbreviated Title.	Journal.
Chem. News	Chemical News.
Chem. Rev. Fett-Harz-Ind.	Chemische Revue über die Fett- und Harz-Industrie.
Chem. Zeit.	Chemiker Zeitung.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Compt. rend. Soc. Biol.	Comptes rendus des Séances de la Société de Biologie.
Electro-Chem. Metall.	The Electro-Chemist and Metallurgist.
Exper. Stat. Record	Experiment Station Record.
Gazzetta	Gazzetta chimica italiana.
Geol. Mag.	Geological Magazine.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
Jahrb. Min. Beil.-Bd.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie. Beilage-Band.
Jahrb. Radioaktiv. Elektronik.	Jahrbuch der Radioaktivität und Elektronik.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Biol. Chem.	Journal of Biological Chemistry, New York.
J. Chim. phys.	Journal de Chimie physique.
J. Geol.	Journal of Geology.
J. Hygiene	Journal of Hygiene.
J. Inst. Brewing	Journal of the Institute of Brewing.
J. Landw.	Journal für Landwirtschaft.
J. Med. Research	Journal of Medical Research.
J. Path. Bact.	Journal of Pathology and Bacteriology.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. Physique	Journal de Physique.
J. pr. Chem.	Journal für praktische Chemie.
J. Roy. Agric. Soc.	Journal of the Royal Agricultural Society.
J. Roy. Soc. New South Wales.	Journal of the Royal Society of New South Wales.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
K. Svenska Vet-Akad. Handl.	Kongl. Svenska Vetenskaps-Akademiens Handlingar.
Landw. Versuchs-Stat.	Die landwirtschaftlichen Versuchs-Stationen.
L'Orosi	L'Orosi.
Mem. Accad. Sci. Torino	Memorie della Reale Accademia delle Scienze di Torino.
Mem. Coll. Sci. Eng. Kyōtō.	Memoirs of the College of Science and Engineering, Kyōtō Imperial University.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Milch Zeit.	Milch Zeitung.
Milch. Zentr.	Milchwirtschaftliches Zentralblatt.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Nuovo Cim.	Il Nuovo Cimento.
Öfver K. Vet.-Akad. Förh.	Öfversigt af Kongl. Vetenskaps-Akademiens Förhandlingar.
Pflüger's Archiv	Archiv für die gesammte Physiologie des Menschen und der Thiere.
Pharm. Arch.	Pharmaceutical Archives.
Pharm. J.	Pharmaceutical Journal.
Pharm. Rev.	Pharmaceutical Review.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).

JOURNALS FROM WHICH ABSTRACTS ARE MADE.

Abbreviated Title.	Journal.
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Proc. Amer. Physiol. Soc.	Proceedings of the American Physiological Society.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. K. Akad. Wetensch. Amsterdam.	Proceedings of the Glasgow Philosophical Society. Proceedings of the Physiological Society.
Proc. Phil. Soc. Glasgow	Koninklijke Akademie van Wetenschappen te Amster-
Proc. Physiol. Soc.	dam. Proceedings (English version).
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Quart. J. Geol. Soc.	Quarterly Journal of the Geological Society.
Rend. Accad. Sci. Fis. Mat. Napoli.	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche-Napoli.
Rev. intern. Falsif.	Revue internationale des Falsifications.
Rec. trav. chim.	Receuil des travaux chimiques des Pays-Bas et de la Belgique.
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of the Royal Dublin Society.
Sci. Trans. Roy. Dubl. Soc.	Scientific Transactions of the Royal Dublin Society.
Sitzungsber. K. Akad. Wiss. Berlin.	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
Sitzungsber. K. Akad. München.	Sitzungsberichte der königlich bayerischen Akademie der Wissenschaften zu München.
Trans. Amer. Inst. Mining Eng.	Transactions of the American Institute of Mining Engineers.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Nova Scotia Inst. Sci.	Transactions of the Nova Scotia Institute of Science.
Trans. Path. Soc.	Transactions of the Pathological Society.
Trans. Roy. Soc. Canada.	Transactions of the Royal Society of Canada.
Trans. Roy. Irish Acad.	Transactions of the Royal Irish Academy.
Tsch. Min. Mitth.	Tschermak's Mineralogische Mittheilungen.
U.S.A. Dept. Agric. Bull.	Bulletins of the Department of Agriculture, U.S.A.
U.S.A. Dept. Agric. Rep.	Reports of the Department of Agriculture, U.S.A.
Wiss. Abhandl. Phys.-Tech. Reichsanstalt.	Wissenschaftliche Abhandlungen der Physikalisch-Technischen Reichsanstalt.
Zeit. anal. Chem.	Zeitschrift für analytische Chemie.
Zeit. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeit. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeit. Biol.	Zeitschrift für Biologie.
Zeit. Elektrochem.	Zeitschrift für Elektrochemie.
Zeit. Farb Text. Ind.	Zeitschrift für Farben- und Textil-Industrie.
Zeit. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie.
Zeit. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeit. öffentl. Chem.	Zeitschrift für öffentliche Chemie.
Zeit. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeit. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Zeit. prakt. Geol.	Zeitschrift für praktische Geologie.
Zeit. Ver. deut. Zuckerind.	Zeitschrift des Vereins der deutschen Zucker-Industrie.
Zeit. Zuckerind. Böhm.	Zeitschrift für Zuckerindustrie in Böhmen.

// JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

Decomposition of Iodoform by the Action of Oxygen and Light Rays. EDMOND VAN AUBEL (*Chem. Centr.*, 1904, ii, 1376; from *Physikal. Zeit.*, **5**, 637. Compare Hardy and Willcock, Abstr., 1903, ii, 622).—Mixtures of iodoform with substances which are not liquid, such as vaselin, are decomposed by sunlight and by radium rays, but when exposed to moderate light in winter at $-45°$, no decomposition could be detected. E. W. W.

Preparation of Di-iodoacetylene. HEINRICH BILTZ and ERNST KÜPPERS (*Ber.*, 1904, **37**, 4412—4416).—The formation of di-iodoacetylene by the interaction of calcium carbide with iodine dissolved in aqueous potassium iodide (Biltz and Werner, Abstr., 1897, i, 389) is due to the calcium hypoiodite, which is produced by the action of calcium hydroxide on iodine, rendering possible a direct substitution by iodine of the hydrogen of acetylene. This is shown by the fact that a good yield of di-iodoacetylene is obtained by passing acetylene gas through ice-cold aqueous potassium hydroxide to which a solution of iodine in aqueous potassium iodide is gradually added. That the hypoiodite itself does not act on the acetylene is proved by the fact that no action takes place on passing the gas through a cold solution of iodine in aqueous sodium hydroxide containing sodium hypoiodite and sodium iodide. W. A. D.

Action of Acetylene on Solutions of Mercuric Chloride. Trichloromercuriacetaldehyde. HEINRICH BILTZ and OTTO MUMM (*Ber.*, 1904, **37**, 4417—4427).—The white precipitate which is formed on passing purified acetylene through mercuric chloride solution has not the composition $C_2Cl_2Hg_2$, as assumed by Keiser (Abstr., 1894, i, 61), but is a trichloromercuriacetaldehyde, $C(HgCl)_3 \cdot CHO$; this is shown by analysis, by the fact that in its formation, according to the equation $C_2H_2 + 3HgCl_2 + H_2O = C_2HOCl_3Hg_3 + 3HCl$, three mols. of hydrogen chloride are eliminated, and by its giving acetaldehyde when boiled with hydrochloric acid. The substance supposed by Hofmann (Abstr., 1899, i, 485) to be $C_2Cl_4Hg_3$ is really the same substance. Chlorine water converts trichloromercuriacetaldehyde into mercuric chloride and chloral. The action of iodine is, however, different; using iodine and water or a solution of iodine in aqueous potassium iodide, three atoms of the halogen are absorbed per molecule; with alcoholic iodine, an absorption of 6 atoms is observed. In each case, mercuric iodide was formed, but other products were not isolated. Potassium permanganate in presence of sulphuric acid oxidises trichloromercuriacetaldehyde directly to mercuric salts and carbon dioxide; the formation of trichlorimercuriacetic acid (Hofmann, Abstr., 1898, i, 635) was not observed.

The compound formed by the interaction of allylene with mercuric chloride (Kutscheroff, Abstr., 1884, 572 and 719) is *trichloromercuriacetone*, $CH_3 \cdot CO \cdot C(HgCl)_3$; it is decomposed by acids giving acetone. Ethylacetylene and mercuric chloride similarly give *trichloromercurimethyl ethyl ketone*. The salt formed by the action of mercuric acetate on allylene is *mercuriacetone acetate*, $Hg{:}CAc \cdot Hg \cdot O \cdot CO \cdot CH_3$.

W. A. D.

Action of Acetylene on Mercuric Chloride Solution. KARL A. HOFMANN (*Ber.*, 1904, **37**, 4459—4460. Compare Abstr., 1898, i, 635; 1899, i, 97, 485; Biltz and Mumm, preceding abstract).—The compound $C_2Hg_3Cl_4$ is hydrolysed by water so rapidly to the aldehyde, $C(HgCl)_3 \cdot COH$, that a preparation free from oxygen could not be obtained. When warmed with an aqueous solution of potassium cyanide, trichloromercurialdehyde yields aldehyde-resin, mercuric cyanide, and mercury.

No precipitate is formed when acetylene is passed through an aqueous solution of mercuric chloride containing a large excess of sodium chloride.

G. Y.

Formation of Alcohols by Reduction of Acid Amides. II. RUDOLF SCHEUBLE and EMMO LOEBL (*Monatsh.*, 1904, **25**, 1081—1105. Compare Abstr., 1904, i, 466).—Reduction with sodium and amyl alcohol of acetamide, heptoamide, and azelamide leads to the formation of ethyl alcohol, heptyl alcohol, and nonane-$\alpha\iota$-diol respectively. *n*-Valeramide, α-methylbutyramide, and $\alpha\alpha$-dimethylpropionamide are reduced to *n*-amyl alcohol, *sec*-butylcarbinol, and *tert.*-butylcarbinol respectively. *n*-Valeramide and $\alpha\alpha$-dimethylpropionamide have been reduced also by sodium in octyl-alcoholic solution to the corresponding

alcohols. In each case, the formation of the alcohol is accompanied by that of the corresponding amine.

Nonane-αι-diol (*enneamethylene glycol*) melts at 45·5° and boils at 177° (corr.) under 15 mm. pressure; the *diacetate*, $C_9H_{18}(OAc)_2$, boils at 161° under 9 mm. pressure; oxidation of the glycol with potassium permanganate in slightly alkaline aqueous solution leads to the formation of azelaic acid. *Nonane-αι-diamine* forms a *platinichloride*, $C_9H_2N_2,H_2PtCl_6$. G. Y.

Oxidation of Acetol (Acetylcarbinol). André Kling (*Compt. rend.*, 1904, **139**, 740—742. Compare Abstr., 1900, i, 129; 1901, i, 625; 1903, i, 223; 1904, i, 2, 474; also Nef, following abstract).—When acetol (acetylcarbinol) is oxidised, it yields lactic acid or a mixture of acetic and formic acids according to the nature of the oxidising agent employed. Such oxidising agents as copper hydroxide, ferric hydroxide, mercuric hydroxide, alkaline potassium ferricyanide, and the manganic hydroxides yield chiefly lactic acid with traces of acetic and formic acids, with the probable formation of an acetolate as an intermediate compound; mercuric chloride and copper acetate also yield lactic acid, but the oxidation is much slower and less complete, whilst chromic acid, lead dioxide, nitric acid, barium or sodium peroxide, potassium permanganate, hydrogen peroxide, silver hydroxide, or a mixture of mercuric sulphate and sulphuric acid yield only formic and acetic acids. M. A. W.

Dissociation of the Glycols and of the Glycerols. I and II. John U. Nef (*Annalen*, 1904, **335**, 191—245, 247—333. Compare Abstr., 1901, i, 626; 1902, i, 6).—When passed over pumice stone at 500—560°, glycol yields acetaldehyde, crotonaldehyde, carbon monoxide, methane, and hydrogen. Ethylene oxide at 400—420° yields acetaldehyde and no gaseous products.

At 500°, propylene oxide forms 2 parts of propaldehyde and 1 part of acetone; under the same conditions, propylene glycol forms propaldehyde only. α-Propaldehydesemicarbazone crystallises in glistening, flat needles and melts at 88—90°; the β-modification crystallises in plates and melts at 154°. The action of hydrogen chloride on propylene oxide at −15° leads to the formation of chloro*iso*propylalcohol, which, when distilled with phosphoric oxide, yields a mixture of α- and γ-chloropropylenes. When passed over pumice stone at 450°, trimethylene glycol yields acraldehyde, allyl alcohol, *n*-propyl alcohol, and a little propaldehyde; under the same conditions, allyl alcohol yields a small amount of diallyl oxide.

The formation of formaldehyde, acetaldehyde, acraldehyde and their products with unchanged glycerol, when glycerol is passed over pumice stone at 430—450°, is explained by the assumption that the glycerol dissociates into $OH{\cdot}CH_2{\cdot}CH{<}^{CH_2-}_{O-}$ and

$$OH{\cdot}CH_2{\cdot}CH{<}^{CH_2O-}_{-},$$

which change into acetol and hydracrylaldehyde respectively. The

acetol further dissociates into formaldehyde and acetaldehyde, the hydracrylaldehyde into water and acraldehyde.

When treated with semicarbazide hydrochloride in aqueous potassium carbonate solution, acraldehyde forms 1-*pyrazoline*-1-*carboxylamide*, $NH_2\cdot CO\cdot N<\begin{matrix} N=CH \\ CH_2\cdot CH_2 \end{matrix}$, which crystallises in glistening needles and melts at 171°. *Acetolsemicarbazone*,

$$OH\cdot CH_2\cdot CMe{:}N\cdot NH\cdot CO\cdot NH_2,$$

crystallises in needles and is only sparingly soluble in ether, benzene, chloroform, or water. The *semicarbazone* of hydracrylaldehyde, $C_4H_9O_2N_3$, forms thick crystals and melts at 114°.

When heated at 250—330°, pentaerythritol yields a distillate which, with semicarbazide hydrochloride in potassium carbonate solution forms a semicarbazone. This melts at 183°, and when recrystallised from water forms 5-*methylpyrazoline*-1-*carboxylamide*, which crystallises in glistening needles and melts at 198°. As acraldehyde is converted into crotonaldehyde in alkaline solution, the reaction for crotonaldehyde with semicarbazide must be carried out in slightly acid solution.

Glycerol ether (Zotta, *Annalen*, 1874, **174**, 87) is identical with β-acraldehydeglycerol, $\begin{matrix} CH_2\cdot CH_2\cdot O\cdot CH_2 \\ | \qquad\qquad\quad | \\ CH<\begin{matrix} O\text{——}CH \\ O\text{——}CH_2 \end{matrix} \end{matrix}$; its formation along with the β-modification, and small amounts of acetol and acetaldehydeglycerol, from glycerol when heated with ammonium chloride at 270—330°, is ascribed to conversion of part of the glycerol into α- and β-chlorohydrins, which dissociate, forming acetol and hydracrylaldehyde.

The formation of allyl alcohol when glycerol is heated with oxalic acid is explained by the formation and dissociation of diformin and reduction of the propargyl alcohol formed by the formic acid. When heated with oxalic acid, glycol yields the monoformate and carbon dioxide; trimethylene glycol and oxalic acid form the monoformate of trimethylene glycol and carbon dioxide.

Glycide is obtained by the action of alcoholic potassium hydroxide on α-chlorohydrin; when heated for 5 hours in a sealed tube at 200—220°, it forms a yellow resin, which is easily soluble in water and, when heated, decomposes with evolution of formaldehyde; glycide does not reduce Fehling's solution; when heated with water at 100°, it yields glycerol; with absolute alcohol, it forms the α-ethyl ether of glycerol. α-Nitroglycerol is formed by the action of water on glycide nitrate, but only to a very small extent by the action of dilute nitric acid on glycide (compare Hanriot, *Ann. Chim. Phys.*, 1879, [v], **17**, 118). At 450°, glycide dissociates into carbon monoxide, hydrogen, methane, acetaldehyde, acetol, and traces of acraldehyde.

The reactions of epichlorohydrin are explained by assuming that it dissociates into the "active molecule," $CH_2Cl\cdot CH<\begin{matrix} CH_2- \\ O- \end{matrix}$. Epi-iodohydrin is formed by the action of potassium iodide on epichlorohydrin in alcoholic solution and treatment of the α-di-iodohydrin so formed with aqueous sodium hydroxide; it boils at 62° under 24 mm.

pressure. *Glycide nitrate,* $\overset{O\text{---}}{\underset{CH_2}{|}}\!\!>CH\cdot CH_2\cdot O\cdot NO_2$, formed by the action of silver nitrate on epi-iodohydrin in ethereal solution, boils at 62—64° under 15 mm. pressure, has a sp. gr. 1·324 at 21·3°, decomposes above 200°, and yields α-nitroglycerin when heated with water. *Diglycide ether,* $\overset{O\text{---}}{\underset{CH_2}{|}}\!\!>CH\cdot CH_2\cdot O\cdot CH_2\cdot CH<\overset{O}{\underset{CH_2}{|}}$, formed when epi-iodohydrin is heated with silver oxide and ether at 60—100°, is a colourless oil, boils at 103° under 22 mm. pressure, has a sp. gr. 1·119 at 23°, and when heated with water at 100°, forms *bisdihydroxypropyl oxide,* $[OH\cdot CH_2\cdot CH(OH)\cdot CH_2]_2O$, which boils at 261—262° under 27 mm. pressure. Diglycide ether dissociates at 440—450° with formation of metaformaldehyde, acetaldehyde, and crotonaldehyde.

When passed over pumice stone heated to 450°, glycide ethyl ether yields acetaldehyde, acetol ethyl ether, and an oil which boils at 80—85° under 23 mm. pressure and is perhaps the diethyl ether, $OH\cdot CH(CH_2\cdot OEt)_2$. The semicarbazone of acetol ethyl ether, $C_6H_{13}O_2N_3$, forms a white, crystalline powder and melts at 92°.

The formation of pyruvic acid from glyceric and from tartaric acid, and of phenylacetaldehyde and carbon dioxide from phenylglyceric acid, and the behaviour of αβ-glycols (chlorohydrins, &c.) with zinc chloride and potassium hydrogen sulphate are explained on the assumption of an "ethylidene dissociation"; the second stage, that of isomerisation, may be replaced by addition of the dissociated parts so as to form a mixture of optically active isomerides (Walden, Abstr., 1898, i, 405), thus:

$$2RR'CHX \rightarrow 2RR'C< + 2HX \rightarrow \begin{matrix}R\\R'\end{matrix}\!\!>C<\begin{matrix}H\\X\end{matrix} + \begin{matrix}R\\R'\end{matrix}\!\!>C<\begin{matrix}X\\H\end{matrix}.$$

The action of dilute acids on αβ-glycols is discussed (compare Krassuski, Abstr., 1902, i, 425; Lieben, Abstr., 1902, i, 336).

Acetylcarbinol is best prepared by boiling chloro- or bromo-acetone with anhydrous potassium or sodium formate in methyl-alcoholic solution in a reflux apparatus. It is formed also by hydrolysis of acetylcarbinyl acetate with methyl alcohol at 140°, by hydrolysis of the acetate or formate of *r*-lactic aldehyde with methyl alcohol or water at 180°, and from *r*-α-bromopropaldehyde by the action of potassium formate in boiling methyl-alcoholic solution or by the action of potassium acetate in alcoholic solution at 100°. The polymerisation of acetylcarbinol is prevented by dilution with an equal volume of methyl-alcohol, provided that no trace of acetic or formic acid is present. Acetylcarbinolphenylhydrazone is formed by the action of phenylhydrazine on acetol in presence of sodium hydroxide in aqueous methyl-alcoholic solution; it melts at 106° (m. p. 100—102°; Pinkus, Abstr., 1898, i, 224). The action of sodium hydroxide and phenylhydrazine on dextrose in aqueous methyl-alcoholic solution leads to the formation of acetolosazone, but no acetylcarbinolphenylhydrazone, therefore pyruvic aldehyde, and not acetol, is the intermediate product in the formation of *r*-lactic acid from dextrose by the action of sodium hydroxide. The formation of acetylcarbinol on addition of sodium hydroxide to fused dextrose is due to reduction of the pyruvic aldehyde first formed

by atomic hydrogen. Acetylcarbinolosazone which melts at 150—154° (compare Perkin, Trans., 1891, **59**, 796), is formed by the action of phenylhydrazine on acetylcarbinol, *r*-lactic aldehyde, or pyruvic aldehyde in 50 per cent. acetic acid.

Bisacetylcarbinol dimethyl ether, $OMe\cdot CMe<\begin{smallmatrix}O\cdot CH_2\\CH_2\cdot O\end{smallmatrix}>CMe\cdot OMe$, formed by the action of formic or acetic acid or methyl-alcoholic hydrochloric acid on acetylcarbinol in methyl-alcoholic solution, melts at 127° and boils at 193—194° (m. p. 130°; b. p. 196°; Henry, *Bull. Soc. chim.*, 1883, **39**, 526); it crystallises in monoclinic plates $[a:b:c=1\cdot77246:1:2\cdot00865;\ \beta=84°13']$ and yields acetylcarbinol and methyl alcohol when boiled with dilute hydrochloric acid. Hydroxyacetoxime (Piloty and Ruff, Abstr., 1897, i, 587) boils at 123—125° under 18 mm. pressure. Acetylcarbinyl acetate, formed by the action of glacial acetic acid and sodium acetate on bromoacetone, is an oil with a sweet odour, boils at 73—74° under 18 mm. pressure, and forms an *oxime*, which boils at 118—119° under 16 mm. pressure, and a *semicarbazone*, $C_6H_{11}O_3N_3$, which crystallises in thick, flat needles and melts at 145°. When passed through a tube heated to 430—450°, acetylcarbinyl acetate yields a somewhat volatile oil consisting principally of acetaldehyde with a small amount of crotonaldehyde and acetic acid.

β-Bromopropaldehydeacetal, $CH_2Br\cdot CH_2\cdot CH(OEt)_2$, formed by the action of hydrogen bromide on acraldehyde in alcoholic solution, boils with slight decomposition at 80—90° under 20 mm. pressure, and when warmed with water yields ethyl alcohol and *β-bromopropaldehyde hydrate*, $CH_2Br\cdot CH_2\cdot CH(OH)_2$, which boils at 40—45° under 18 mm. pressure and has sp. gr. 1·36 at 22°. *α-Bromopropaldehyde*, formed by the action of bromine on propaldehyde in acetic acid solution, boils at 42—44° under 63 mm. pressure, has a sp. gr. 1·523 at 21°, and dissolves in water or alcohol with development of heat. *α-Iodopropaldehyde*, obtained by treating α-bromopropaldehyde with a cold saturated solution of potassium iodide, boils at 40° under 15 mm. pressure, and, when heated with silver acetate and ether at 100°, yields the *acetate* of *r*-lactaldehyde, which is an oil of aromatic odour, boils at 55—65° under 19 mm. or at 52—55° under 15 mm. pressure, develops heat when treated with water or alcohol, and is hydrolysed by water at 100° to acetic acid and acetylcarbinol. The *semicarbazone*, $NH_2\cdot CO\cdot NH\cdot N\colon CH\cdot CHMe\cdot OH$, crystallises in flat, glistening needles and melts at 163°.

When heated with acetic anhydride in a sealed tube at 100°, acetylcarbinol yields acetylcarbinyl acetate; benzoylcarbinol and acetic anhydride at 100° form ω-acetoxyacetophenone, which is also formed by the action of ω-bromoacetophenone on silver acetate and is isomeric with mandelaldehyde acetate, obtained from α-bromophenylacetaldehyde, and silver acetate. Acetol and benzoylcarbinol, therefore, are hydroxyketones and are isomeric with lactaldehyde and hydroxyphenylacetaldehyde respectively (compare Kling, Abstr., 1903, i, 138, 223).

Acetylcarbinol reduces cupric hydroxide in aqueous sodium hydroxide solution to cuprous oxide at the ordinary temperature; the resulting

solution contains *r*-lactic acid, but not more than traces of acetic or formic acid. Copper acetate is reduced to cuprous oxide, or copper sulphate to metallic copper, by acetylcarbinol or benzoylcarbinol in aqueous solution; the former yields *r*-lactic acid, the benzoylcarbinol yields, at the ordinary temperature, benzoylformaldehyde, which, when treated with aqueous sodium hydroxide, or when heated with aqueous copper acetate or sulphate solution, is converted into *r*-mandelic acid. A mixture of acetaldehyde and formaldehyde does not reduce cupric hydroxide or copper salts under the same conditions as does acetylcarbinol, the reducing power of which is explained on the assumption of "ethylidene dissociation": $Ac{\cdot}CH_2{\cdot}OH = Ac{\cdot}CH\colon + H_2O$, $Ac{\cdot}CH\colon + 2H_2O = Ac{\cdot}CH(OH)_2 + 2H{\cdot}$; the reduction is caused by the liberated hydrogen, and the acetyl formaldehyde hydrate undergoes isomeric change into *r*-lactic acid. In aqueous or acid solution, acetol dissociates to acetaldehyde and formaldehyde, so that on oxidation with silver oxide, mercuric oxide, or potassium dichromate and sulphuric acid it yields acetic and formic acids and carbon dioxide. Acetylcarbinol, acetylcarbinyl acetate, and chloro- or bromo-acetone react with solid alkali hydroxides with development of heat and formation of a red resin, $(Ac{\cdot}CH)_x$?, which is also formed by the action of 20 per cent. aqueous potassium or sodium hydroxide, or slowly by the action of aqueous sodium carbonate on acetol.

Decompositions of glycerol, sodium glyceroxide, glyceric, lactic, and pyruvic acids, the action of alkali hydroxides on the glycols, and the oxidation of the glycols and of glycerol are discussed from the point of view of the author's dissociation hypothesis.

As glycerol, when heated with 1 mol. of sodium hydroxide, yields propylene glycol, and, when treated with sodium hydroxide and mercuric oxide, forms *r*-glyceric acid, sodium glyceroxide must have the constitution $OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}ONa$. Contrary to statements in the literature, glycerol, when heated with an excess of potash-lime at 260°, yields chiefly carbon dioxide and propionic acid. With *p*-nitrobenzoyl chloride, sodium glyceroxide yields *glyceryl tri*-p-*nitrobenzoate*, which crystallises in colourless needles and melts at 192°, and *di*-p-*nitrobenzoate*, which forms colourless plates and melts at 137°.

When heated with $1\frac{1}{2}$ parts of 15 per cent. aqueous sodium hydroxide in a sealed tube at 40—50°, *r*-glyceraldehyde, dextrose, and lævulose yield the same amounts of *r*-lactic and trihydroxy-*n*-butyric acids. When warmed with dilute sodium hydroxide and cupric hydroxide, *r*-glyceraldehyde yields *r*-glyceric acid, whilst dextrose and lævulose form chiefly trihydroxy-*n*-butyric acid and no glyceric acid. G. Y.

Action of Hydrogen Bromide or Hydrogen Chloride on Triacetin. New Halogen Derivatives of Triacetin. R. DE LA ACEÑA (*Compt. rend.*, 1904, **139**, 867—868).—*αα-Dibromomonoacetin* (*αγ-dibromo-β-acetylglycerol*), $OAc{\cdot}CH(CH_2Br)_2$, obtained by the prolonged action of hydrogen bromide on triacetin, or by heating the mixture at 100° in sealed tubes, boils at 130—135° under 40 mm. pressure, has a sp. gr. 1·5880 at 15°, has an agreeable aromatic odour, is slightly soluble in water, and readily so in alcohol or ether, and yields *iso*propyl alcohol on reduction. *α-Bromodiacetin* (*α-bromo-βγ-*

diacetylglycerol), $CH_2Br\cdot CH(OAc)\cdot CH_2\cdot OAc$, produced by the prolonged action of an acetic acid solution of hydrogen bromide on an ethereal solution of triacetin at 0° in the dark, boils at 150—155° under 40 mm. pressure, has a sp. gr. 1·2905 at 15°, and yields *iso*propylene glycol on reduction. *αα-Dichloromonoacetin* (*αγ-dichloro-β-acetylglycerol*), prepared similarly to the bromine compound, boils at 115—120° under 40 mm. pressure and has a sp. gr. 1·1618 at 15°. *α-Chlorodiacetin* (*α-chloro-βγ-diacetylglycerol*) boils at 145—150° under 40 mm. pressure and has a sp. gr. 1·1307 at 15°. *αβ-Dichloromonoacetin*, prepared by the action of acetic anhydride on chlorinated allyl alcohol, has a sp. gr. 1·1677 at 15°, but in all other respects is identical with the *αα*-isomeride. *α-Iododiacetin*, obtained by the action of sodium iodide on the corresponding chlorine compound, is an unstable oil having a sp. gr. 1·4584 at 15°. M. A. W.

Resemblance between Iron Salts of Organic Acids and Salts of Nitro-derivatives. Michael I. Konowaloff (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 1062—1067).—All the monobasic organic acids give ferric salts which dissolve in ether with formation of a red coloration similar to that given by primary and secondary nitro-derivatives. The sensitiveness of the reaction is less with the organic acids than with the nitro compounds ; in applying the test to the latter substances, it is necessary to get rid of any free acid by means of soda. The ferric salts of the organic acids are formed to a slight extent by the action of ferric chloride, hydroxide, or basic carbonate on the free acid in aqueous solution. They are formed more readily by the interaction of the free organic acid and iron reduced by hydrogen, and still more readily by the action of ferric chloride on the free acid in aqueous alcoholic solution. T. H. P.

[Electrolysis of Potassium Acetate.] Hans Hofer and M. Moest (*Zeit. Elektrochem.*, 1904, **10**, 833—834).—Foerster and Piguet (Abstr., 1904, i, 965) appear to have overlooked the authors' paper (Abstr., 1902, i, 736), in which it was shown that methyl alcohol is always formed in the electrolysis of potassium acetate. This formation of methyl alcohol accounts for the deficit of ethane observed, and also for the formation of carbon dioxide, without assuming the anodic oxidation of acetic acid, a reaction which it has been proved does not take place to any appreciable extent in acid solutions. T. E.

Composition of Homologues of "Schweinfurt's Green." Georges Viard (*Bull. Soc. chim.*, 1904, iii, **31**, 1138—1142).—A series of homologues of this pigment have been prepared using formic, propionic, and *n*- and *iso*butyric acids in place of acetic acid. They closely resemble Schweinfurt's green in appearance and properties (the formic acid derivative decomposes above 170° and the others above 200°, evolving arsenious oxide), and have compositions corresponding with the typical formula $CuAc_2,3Cu(AsO_2)_2$ (compare Wöhler and Springmann, *Annalen*, 1855, **94**, 44, and Abraham, *Chem. News*, 1870, **21**, 265). These products are best obtained when precipitation is carried out in presence of a small quantity of the respective organic acid. When there is no free acid present, the true Schweinfurt's green is only formed in the later stages, and the first products are

yellowish-green substances, richer in copper and poorer in arsenic than the true pigments. The latter, even when produced at the ordinary temperature do not contain water of crystallisation. T. A. H.

β-Bromobutyric Acid. ROBERT LESPIEAU (*Compt. rend.*, 1904, **139**, 738—739).—*β-Bromobutyramide*, $CHMeBr\cdot CH_2\cdot CO\cdot NH_2$, prepared by the action of hydrobromic acid on allyl cyanide in the cold, crystallises from boiling chloroform in white crystals melting at 92—93°, and is converted into crotonamide, $CHMe\!:\!CH\cdot CO\cdot NH_2$, by the action of normal potassium hydroxide solution. *β-Bromobutyric acid*,

$$CHMeBr\cdot CH_2\cdot CO_2H,$$

prepared by hydrolysing the corresponding amide by means of warm hydrobromic acid, melts at 17—18° and boils at 122° under 16 mm. pressure; the *ethyl* ester, prepared by saturating an alcoholic solution of the acid with hydrobromic acid, boils at 183° under 755 mm. pressure; α-bromobutyric acid melts at $-4°$ and boils at 114—115° under 20 mm. pressure. β-Bromobutyric acid loses HBr by the action of potassium hydroxide, and is converted into crotonic acid. These facts afford direct evidence in favour of Pinner's explanation of the formation of crotonic acid from allyl cyanide (compare Abstr., 1880, 99). M. A. W.

Synthesis of Nitro-esters. CELSO ULPIANI (*Atti R. Accad. Lincei*, 1904, [v], **13**, ii, 346—349).—In the method previously described by the author (Abstr., 1903, i, 791) for the synthesis of nitro-esters from ethyl nitromalonate, the yield obtained diminishes as the molecular weight of the alkyl iodide employed increases. Even in the case of ethyl α-nitrobutyrate, it is best not to use this method of synthesis, but to nitrate ethyl ethylmalonate directly and then to decarboxylate by means of sodium ethoxide. The latter method is generally applicable where the conditions of complete nitration of the ethyl alkylmalonate are known. Ethyl ethylmalonate, for example, is completely nitrated by standing for 48 hours in contact with fuming nitric acid, yielding ethyl nitromalonate, which, when treated with sodium ethoxide and the solution acidified, gives *ethyl α-nitrobutyrate*, $CHEt(NO_2)\cdot CO_2Et$, as an oil boiling at about 123° under 20 mm. pressure. The *sodium* derivative is readily soluble in water, alcohol, ethyl acetate, and acetone, and the *ammonium* compound crystallises in nacreous laminæ, which in a desiccator lose ammonia and liquefy.

T. H. P.

Action of Iodine and Yellow Oxide of Mercury on Acids containing an Ethylenic Linking. Separation of Isomerides. J. BOUGAULT (*Compt. rend.*, 1904, **139**, 864—867. Compare Abstr., 1900, i, 495, 641; 1901, i, 383).—Unsaturated acids of the type $CHR\!:\!CH\cdot CO_2H$, containing the ethylenic linking in the $\alpha\beta$-position, and of the type $CH_2\!:\!CR\cdot CO_2H$, do not react with iodine and yellow mercuric oxide (nascent hypoiodous acid); the acids containing the ethylenic linking in the $\beta\gamma$ position react readily with hypoiodous acid to form the corresponding iodo-lactone of the type

$$CHI{<}{\begin{matrix}CH_2\cdot CO\\ -CHR-\end{matrix}}{>}O,$$

which is insoluble in alkalis, generally crystalline, and the yield is quantitative. Hypoiodous acid is, therefore, a convenient reagent for separating $\beta\gamma$-unsaturated acids from their $\alpha\beta$-isomerides, and 0·01 gram of hydropiperic ($\beta\gamma$) or hydrosorbic ($\beta\gamma$) acid was thus separated from 3 or 4 grams of the $\alpha\beta$-isomeride. Unsaturated acids of the type $CHR\dot{:}CH\cdot[CH_2]n\cdot CO_2H$ ($n > 2$) react readily with hypoiodous acid to form saturated compounds having the formula $OH\cdot CHR\cdot CHI\cdot[CH_2]n\cdot CO_2H$ or $CHRI\cdot CH(OH)\cdot[CH_2]n\cdot CO_2H$.

M. A. W.

Drying Process of Linseed Oil. Wilhelm Fahrion (*Chem. Zeit.* 1904, **28**, 1196—1200. Compare Abstr., 1904, ii, 217).—An historical survey of work done on the chemical changes involved during the drying of linseed oil. The subject is discussed from the point of view of Engler's auto-oxidation theory.

A. McK.

Elæomargaric Acid. Moritz Kitt (*Chem. Rev. Fett. Ind.*, 1904, **11**, 190).—Elæomargaric acid, obtained from the fruit of *Aleurites cordata*, changes after a few hours' exposure to air, being gradually oxidised to a resin. When oxidised by alkaline permanganate, it forms traces of dihydroxystearic acid, whilst a solid fatty acid, melting between 97° and 102°, together with considerable amounts of volatile fatty acids, is also produced.

A. McK.

Preparation of α-Ketonic Acids and Esters from α-Oximino-esters. (Part V.) Louis Bouveault and René Locquin (*Bull. Soc. chim.*, 1904, iii, **31**, 1142—1147. Compare Abstr., 1904, i, 849).—The α-oximino-esters of the type $NOH\dot{:}CR\cdot CO_2Et$ (*loc. cit.*) are partially hydrolysed into the corresponding ketonic esters by heating in sealed tubes with hydrogen chloride dissolved in alcohol, but the separation of the products from this liquid is difficult. The results of a number of experiments with oxidising agents having for their object the elimination of the oximino-group show that products capable of yielding nitrous acid are most suitable for the purpose. The following method is recommended. The oximino-ester is dissolved in twice its weight of formic acid containing 15 per cent. of water and ether sufficient to form a layer added. The whole is cooled to 0°, and the requisite quantity of nitrosylsulphuric acid added gradually, so that the temperature does not rise beyond 25—30°. The liquid is cooled and poured into five times its weight of ice, and the ethereal layer separated, washed with a little water, dried, and the ether distilled off. The residue, after the removal of formic acid by fractional distillation, contains some unchanged α-oximino-ester, in addition to the required α-ketonic ester and any free acid produced by the hydrolysis of the latter (the butyl- and amyl-esters are most resistant to hydrolysis). The free acid is removed by agitation with a dilute solution of sodium carbonate, and the unchanged oximino-ester by fractional distillation.

From the α-ketonic esters so prepared, the acids are obtained by heating with water in sealed tubes at 150—160° (compare Bouveault and Wahl, Abstr., 1901, i, 252), but in the case of the hexyl and higher esters saponification with alkaline solutions may be resorted to.

T. A. H.

α-Ketonic Acids and Esters (Homopyruvic Compounds). RENÉ LOCQUIN (*Bull. Soc. chim.*, 1904, [iii], 31, 1147—1153. Compare Abstr., 1904, i, 849 and preceding abstract).—These esters are colourless or slightly yellow liquids, readily saponified by alkalis, and in the case of the first members of the series by water alone. The acids distil under reduced pressure. The melting points recorded below were determined on the mercury-bath. The following products have usually been prepared by the methods described in the preceding abstract.

Ethyl α-ketobutyrate, $COEt·CO_2Et$ (compare Aristoff and Demjanoff, Abstr., 1888, 251), obtained in minute quantity by the prolonged action of hydrochloric acid on a mixture of ethyl ethylbutyrylacetate and sodium nitrite dissolved in water, is very soluble in water, boils at 75° under 20 mm. pressure, and at 162° under 760 mm. pressure.

Ethyl α-ketovalerate is obtained to the extent of 10—15 per cent. by the general method, the remainder being hydrolysed; it boils at 72—77° under 10 mm. pressure and furnishes a crystalline *semicarbazone* which melts at 139—140° (corr.). The corresponding acid was characterised by its phenylhydrazone (compare Brunner, Abstr., 1895, i, 335).

iso*Butyl α-ketovalerate*, of which a yield of 30 per cent. was obtained, boils at 87—88° under 11 mm. pressure, has sp. gr. 0·973 at 0°/4°; the *semicarbazone* separates from benzene and light petroleum in spangles, becomes anhydrous at 90°, and melts at 137—138° (corr.). *Ethyl α-keto*iso*hexoate* boils at 74° under 11 mm. pressure and at 93° under 25 mm. pressure, the *semicarbazone* crystallises in spangles and melts at 158—159° (corr.). The corresponding *acid*, prepared by the general method (Bouveault and Wahl, Abstr., 1901, i, 252), boils at 84—85° under 15 mm. pressure and melts at −1·5°; the *semicarbazone*, which is a slightly soluble powder, melts at 205° (corr.). *Ethyl α-keto*iso*heptoate*, a liquid of agreeable odour, boils at 93—94° under 12 mm. pressure, and has sp. gr. 0·979 at 0°/4°; the *semicarbazone* crystallises from a mixture of alcohol and benzene in spangles and melts at 162—163° (corr.); the corresponding acid (compare Fittig and Kaehlbrandt, Abstr., 1899, i, 418) was obtained by hydrolysing the ester with a dilute solution of potassium hydroxide; the *semicarbazone* crystallises from dilute alcohol and melts and decomposes at 205·5° (corr.).

Ethyl α-keto-β-methylnonoate, $C_6H_{13}·CHMe·CO·CO_2Et$, a mobile liquid, boils at 123—124° under 12 mm. pressure, and has a sp. gr. 0·944 at 0°/4°; the *semicarbazone* is amorphous; the corresponding *acid* is a slightly viscous oil boiling at 124—125° under 9 mm. pressure, has sp. gr. 0·991 at 0°/4°, and yields a *semicarbazone* which crystallises from benzene and melts at 121—121·5° (corr.).

T. A. H.

Hydrogenation of Esters of Unsaturated Acids. LOUIS BOUVEAULT and GUSTAVE BLANC (*Bull. Soc. chim.*, 1904, [iii], 31, 1206—1210. Compare Abstr., 1903, i, 597, 673; 1904, i, 642). —The esters of unsaturated acids are readily reduced to the corresponding unsaturated primary alcohols by sodium and absolute alcohol,

except in cases where the ethylenic linking occupies the $\alpha\beta$-position with reference to the carboxyl group. In the latter case, the corresponding saturated primary alcohols are produced, thus affording, in conjunction with Reformatsky's method of condensing aldehydes and ketones with α-halogenated acids to form $\alpha\beta$-unsaturated acids, a convenient method of preparing complex alcohols of the type $CH_2R \cdot CHR' \cdot CH_2 \cdot OH$ and $CHRR' \cdot CHR'' \cdot CH_2 \cdot OH$.

Ethyl β-hydroxy-β-methylnonoate, $C_6H_{13} \cdot CMe(OH) \cdot CH_2 \cdot CO_2Et$, prepared by condensing methyl hexyl ketone with ethyl iodoacetate in presence of zinc or magnesium, is a colourless, slightly viscous liquid, which boils and decomposes at 138° under 17 mm. pressure; when dissolved in acetic acid and boiled with zinc chloride, it yields *ethyl β-methyl-Δ^α-nonenoate*, $C_6H_{13} \cdot CMe{:}CH \cdot CO_2Et$; this is a colourless liquid, which boils at 119—120° under 14 mm. pressure and has a sp. gr. 0·907 at 0°/4°, and on reduction furnishes *γ-methylnonyl alcohol*, $C_6H_{13} \cdot CHMe \cdot CH_2 \cdot CH_2 \cdot OH$, which is a mobile liquid boiling at 111—116° under 14 mm. pressure and having a sp. gr. 0·856 at 0°/4°.

The same cycle of operations applied to methylheptanone gives rise in turn to *ethyl β-hydroxy-βζ-dimethyloctoate* and *ethyl βζ-dimethyl-Δ^α-octenoate* (*β-isohexylcrotonate*), the latter on reduction gives *γη-dimethyloctyl alcohol* (dihydrorhodinol, or citronellol, or tetrahydrogeraniol), a colourless liquid of pleasant odour, boiling at 118° under 15 mm. pressure and having a sp. gr. 0·849 at 0°/4°; the *pyruvate* boils at 140—145° under 13 mm. pressure (compare Bouveault, Abstr., 1904, i, 465). Cinnamic acid on reduction gives rise to γ-phenylpropyl alcohol, which boils at 235°. Ethyl oleate, on reduction, gives *oleyl alcohol* mixed with elaidyl alcohol?; this is a colourless, viscous liquid, which boils at 200° under 13 mm. pressure and has a sp. gr. 0·862 at 0°/4°, and furnishes a *phenylurethane*, apparently not homogeneous, which melts at 38°. Undecenoic acid gives the corresponding *alcohol*; this is a colourless, mobile liquid, which boils at 132—133° under 15 mm. pressure and has a sp. gr. 0·860 at 0°/4°; the *phenylurethane* crystallises well and melts at 55°. T. A. H.

Hydrogenation of Esters of Acids with an Acetal Function. Louis Bouveault and Gustave Blanc (*Bull. Soc. chim.*, 1904, [iii], **31**, 1210—1213).—The esters of hydroxy- and amino-acids are not reduced by sodium and alcohol. For the preparation of glycols, the authors have therefore had recourse to the reduction of esters of alkyloxy-acids of the type $OR \cdot CH_2 \cdot CO_2Et$. The position of the OR-group with reference to the carboxyl group exerts a considerable influence on the course of this reaction. When it is in the α-position, it is replaced by an atom of hydrogen forming a simple alcohol, whereas when it occupies the β-position normal reduction takes place with the formation of a monoalkyl glycol. Ethyl β-ethoxypropionate furnishes the *monoethylin* of *trimethyleneglycol*, $OEt \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OH$; this is a colourless liquid, which is soluble in water, boils at 160°, and has a sp. gr. 0·936 at 0°/4°; the *pyruvate-semicarbazone* is crystalline and melts at 127—128°.

Ethyl β-ethoxycrotonate, $OEt \cdot CMe{:}CH \cdot CO_2Et$, furnishes on reduction

butyric acid and a neutral *compound*, $OEt\cdot CHMe\cdot CH_2\cdot CH_2\cdot OH$, which boils at 168°.

Propyl γγ-diethoxyvalerate, $CMe(OEt)_2\cdot CH_2\cdot CH_2\cdot CO_2Pr^a$, prepared by condensing propyl lævulate with ethyl iminoformate hydrochloride in presence of alcohol, is a colourless liquid, boils at 115—120° under 15 mm. pressure, and on reduction yields a small quantity of a neutral *product* ($C_9H_{20}O_3$?) which boils indefinitely between 140° and 170°. T. A. H.

Reduction of Esters of Hydroxy- and Ketonic Acids. Louis Bouveault and Gustave Blanc (*Bull. Soc. chim.*, 1904, [iii], **31**, 1213—1216. Compare preceding abstract).—Ethyl β-hydroxy-β-methylnonoate on reduction with sodium and absolute alcohol furnishes Bouis's octyl alcohol (β-octanol) and the pinacone corresponding with methyl hexyl ketone. Ethyl β-hydroxydihydrogeranate (Barbier and Bouveault, Abstr., 1896, i, 445) behaves similarly, yielding methylheptenol and the corresponding pinacone; ethyl β-hydroxy-β-phenylpropionate furnishes coumaric acid.

The esters of pyruvic and lævulic acids when reduced in this way do not yield well defined products, but better results are obtained with the β-ketonic esters; thus ethyl α-*iso*butylacetoacetate yields *iso*hexyl alcohol and *iso*hexoic acid; ethyl α-allylacetoacetate furnishes Δ^ϵ-pentenyl alcohol, which boils at 139—142° and has a sp. gr. 0·863 at 0°/4°, and ethyl methylpropylacetoacetate gives β-methylamyl alcohol, which boils at 146—148° and has an odour like that of amyl alcohol. T. A. H.

γδ-Dihydroxypropylmalonic Acid. Wilhelm Traube (*Ber.*, 1904, **37**, 4540—4544).—Bromine reacts with an acetic acid solution of Traube and Lehmann's dihydroxypropylmalonamide (Abstr., 1899, i, 417; 1901, i, 501) yielding ammonium bromide and the *amide* of *α-bromo-δ-hydroxyvalerolactone-α-carboxylic acid*,

$$\begin{matrix} CH_2\cdot CBr(CO\cdot NH_2) \\ | \\ CH(CH_2\cdot OH)—O \end{matrix}\!\!>CO.$$

This latter is readily soluble in all solvents, but may be crystallised from ethyl acetate in the form of colourless prisms melting at 109°. It readily reacts with concentrated ammonia yielding the *amide* of *3-hydroxytetrahydrofuran-1 : 1-dicarboxylic acid*,

$$\begin{matrix} CH_2\cdot C(CO\cdot NH_2)_2 \\ | \\ CH(OH)——CH_2 \end{matrix}\!\!>O,$$

which yields the free *acid* on hydrolysis with sodium hydroxide. This acid is most readily purified by means of its *lead* salt, which is only sparingly soluble in water; the acid crystallises from water in large cubes containing $1H_2O$, which it loses at 130°. When the aqueous solution is heated at 150—160°, carbon dioxide is evolved and *3-hydroxytetrahydrofuran-1-carboxylic acid* is obtained. This crystallises in well developed prisms and melts at 110°. J. J. S.

Anhydrides of Saturated Dibasic Acids and Baeyer's Tension Theory. Gerardus L. Voerman (*Rec. Trav. Chim.*, 1904, **23**, 265—282).—The conclusions arrived at have already been given

(Abstr., 1904, i, 287). The present paper contains details of the experimental work. T. A. H.

Action of Pyridine and Quinoline Bases on Bromosuccinic and Dibromosuccinic Esters. LOUIS DUBREUIL (*Compt. rend.*, 1904, **139**, 870—871. Compare Abstr., 1904, i, 189).—Ethyl bromosuccinate is converted quantitatively into methyl fumarate boiling at 215—220° and melting at $-2°$ by the direct action of excess of pyridine, quinoline, or quinaldine, the hydrogen bromide uniting with the excess of the base to form pyridine hydrobromide, C_5H_5NHBr, melting at 191°, *basic quinoline hydrobromide*, $(C_9H_7N)_2,HBr,2H_2O$, melting at 41°, and *basic quinaldine hydrobromide*, melting at 54°, respectively; all these salts are deliquescent, and the two last are decomposed by water. Ethyl dibromosuccinate is converted into ethyl bromomaleate by the action of quinoline or quinaldine, the basic hydrobromides of the bases being formed at the same time, and into ethyl acetylenedicarboxylate by the action of pyridine. M. A. W.

Solubility of the Tartrates of the Alkaline Earths in Water. H. CANTONI and Mlle. ZACHODER (*Bull. Soc. chim.*, 1904, [iii], **31**, 1121—1124).—The solubilities of calcium tartrate, $CaC_4H_4O_6,4H_2O$, strontium tartrate, $SrC_4H_4O_6,3H_2O$, and barium tartrate, $BaC_4H_4O_6$, have been determined at various temperatures between 0° and 60°. The results show that in all three cases the solubility increases with rise of temperature and that the strontium salt is most, and the barium salt least, soluble at the same temperature. The results are tabulated in the original. It is suggested that in the manufacture of tartaric acid this might, with advantage, be precipitated as the barium salt, since this is less soluble than the calcium salt now generally employed. T. A. H.

Thioformic Acid. VICTOR AUGER (*Compt. rend.*, 1904, **139**, 798—800).—In order to obtain thioformic acid, the action of sulphide of phosphorus on formic acid, and the saponification of phenyl formate by sodium hydrosulphide have been investigated. Phosphorus pentasulphide has no action on formic acid, even at its boiling point, but sodium metathiophosphate, prepared by fusing 1 mol. of phosphorus pentasulphide with 1 mol. of sodium sulphide, reacts readily. On distilling the product in a vacuum, a mixture of formic and thioformic acids collects in the receiver, from which the formic acid can be separated by cooling to $-20°$. The remaining liquid is very unstable, gives off hydrogen sulphide, and deposits a white, amorphous substance. Its properties indicate the presence of thio-acid, but this could not be obtained pure.

Phenyl formate reacts readily with sodium hydrosulphide in absolute alcoholic solution, $HCO_2 \cdot C_6H_5 + NaHS = HCO \cdot SNa + C_6H_5 \cdot OH$. After removal of the alcohol, ether precipitates the sodium salt in the form of long, white, very deliquescent needles, which are mixed with excess of formic acid and distilled in a vacuum. The thioformic acid is collected in a receiver cooled by methyl chloride; it decomposes very rapidly.

Phenyl formate, which usually contains considerable quantities of

phenol, can be purified by converting the latter into the less volatile phenyl benzoate by means of benzoyl chloride in presence of pyridine, the temperature being kept below 10°, when most of the phenyl benzoate crystallises. Pure phenyl formate boils at 107° under 25 mm. and at 173° under 760 mm. pressure; it solidifies at $-45°$, is highly refractive, and has a sp. gr. 1·0879 at 0°. H. M. D.

Synthesis of ββ-Dimethyladipic Acid. GUSTAVE BLANC (*Compt. rend.*, 1904, **139**, 800—802).—Reduction of ββ-dimethylglutaric anhydride gives a lactone, $CMe_2<\substack{CH_2-CO \\ CH_2\cdot CH_2}>O$, which resembles camphor in appearance, melts at 34°, and boils at 234°. When heated with potassium cyanide at 275° and the product hydrolysed, an acid is obtained which most probably is ββ-dimethyladipic acid,

$$CO_2H\cdot CH_2\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CO_2H.$$

It is very soluble in water, insoluble in light petroleum, melts at 87—88°, and is identical with Tiemann's ββ-dimethyladipic acid obtained by the oxidation of α-ionone (compare Abstr., 1898, i, 377). The acid obtained by Noyes (Abstr., 1901, i, 631), by condensing the ethyl ester of γ-bromo*iso*hexoic acid with ethyl sodiomalonate and hydrolysing the product, which he represented as ββ-dimethyladipic acid, is, on the other hand, only slightly soluble in water, and melts at 102°. The author comes to the conclusion that in Noyes's synthesis an intramolecular change takes place. H. M. D.

Action of Potassium Ethyl Xanthate on Monohalogen Substituted Fatty Acids and their Derivatives. JULIUS TRÖGER and FRANZ VOLKMER (*J. pr. Chem.*, 1904, [ii], **70**, 442—448. Compare Cech and Steiner, *Ber.*, 1875, **8**, 902).—Ethyl xanthoacetamide,

$$NH_2\cdot CO\cdot CH_2\cdot S\cdot CS\cdot OEt,$$

obtained by the action of chloroacetamide on potassium ethyl xanthate in alcoholic solution, crystallises in glistening leaflets, melts at 114°, and is soluble in alcohol or hot water. Bromine acts towards ethyl xanthoacetamide in neutral or acetic acid solution as an oxidising agent, sulphuric acid being formed.

Ethyl xanthoacetonitrile, $CN\cdot CH_2\cdot S\cdot CS\cdot OEt$, obtained from potassium ethyl xanthate and chloroacetonitrile, is a mobile yellow oil, which is soluble in ether or alcohol and is decomposed by hydrogen sulphide in alcoholic ammoniacal solution, or by hydrogen chloride in benzene solution. When heated with hydroxylamine hydrochloride and sodium carbonate in aqueous alcoholic solution, ethyl xanthoacetonitrile is decomposed with formation of resinous products.

Methyl ethyl xanthoacetate, $OEt\cdot CS\cdot S\cdot CH_2\cdot CO_2Me$, obtained from potassium ethyl xanthate and methyl chloroacetate, is a yellow oil. When shaken with 10 per cent. aqueous ammonia, it dissolves, and on evaporation of the solution yields a white substance, probably a mixture of the amide and the ammonium salt.

Propyl ethyl xanthoacetate, $OEt\cdot CS\cdot S\cdot CH_2\cdot CO_2Pr$, is a yellow oil, which, when shaken with aqueous ammonia, yields the *ammonium* salt.

Diethyl xanthoacetoacetate, $OEt\cdot CS\cdot S\cdot CHAc\cdot CO_2Et$, is a mobile, red oil; it is decomposed by the action of phenylhydrazine in alcoholic

solution, but without formation of phenylmethylpyrazoloneketophenylhydrazone (see this vol., i, 89).

Ethyl xantho-α-propionic acid, $OEt\cdot CS\cdot S\cdot CHMe\cdot CO_2H$, obtained from potassium ethyl xanthate and α-bromopropionic acid, is a green oil. *Ethyl xantho*iso*butyric acid* is a mobile yellow oil. *Diethyl xantho-α-butyrate*, $OEt\cdot CS\cdot S\cdot C_3H_6\cdot CO_2Et$, is a viscid, yellow oil. *Ethyl xanthoacetone*, $OEt\cdot CS\cdot S\cdot CH_2Ac$, is a dark brown oil.

Methyl xanthoacetamide, $OMe\cdot CS\cdot S\cdot CH_2\cdot CO\cdot NH_2$, crystallises in white, glistening scales and melts at 119°. G. Y.

Sulpho*iso*butyric Acid. J. Moll van Charante (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 7, 275—277).—*Sulpho*iso*butyric acid*, $SO_3H\cdot C_3H_6\cdot CO_2H$, prepared by the action of sulphuric acid (1 mol.) on *iso*butyric anhydride (2 mols.), contains $2H_2O$ and is very hygroscopic. Its *barium* salt contains $3H_2O$ and its *sodium* salt $\frac{1}{2}H_2O$. By the action of phosphorus pentachloride on the sodium salt, the *dichloride* may be obtained as a colourless liquid which boils at about 55° under 1—0·5 mm. pressure and solidifies at −10°. It has n_D 1·4887 and the sp. gr. 1·4696 at 20°/4°. By varying the conditions of the action of phosphorus pentachloride on the sodium salt, a chloroanhydride, melting at 61°, may also be obtained.

With a little water, the dichloride yields *chlorosulpho*iso*butyric acid*, $SO_2Cl\cdot C_3H_6\cdot CO_2H$, which melts at 134°, whilst with more water sulpho*iso*butyric acid is produced. By the action of methyl alcohol on the dichloride, *methyl chlorosulpho*iso*butyrate* is formed; it boils at about 60° under 1·5 mm. pressure and solidifies at 21·5°; it has the sp. gr. 1·3436 at 20°/4° and n_D 1·46658.

The *dimethyl* ester, $SO_3Me\cdot C_3H_6\cdot CO_2Me$, formed from methyl iodide and the normal silver salt, boils at 78—82° under 0·5—1 mm. pressure and melts at 4°. It has the sp. gr. 1·2584 at 20°/4° and n_D 1·44481.

*Methyl sulpho*iso*butyrate*, $SO_3H\cdot C_3H_6\cdot CO_2Me$, prepared by the action of hydrogen chloride and methyl alcohol on sodium sulpho*iso*butyrate, is hygroscopic. The isomeric hydrogen ester, *methyl-sulpho*iso*butyric acid*, $SO_3Me\cdot C_3H_6\cdot CO_2H$, melts at 90°. A. McK.

The Aldol from Synthetic *iso*Propylacetaldehyde [*iso*Valeraldehyde]. J. Rainer (*Monatsh.*, 1904, **25**, 1035—1050. Compare Kohn, Abstr., 1896, i, 10, 461; 1897, i, 396).—*iso*Amyl alcohol is best prepared by the action of *iso*butyl bromide and magnesium on trioxymethylene in ethereal solution and treatment of the product with water; it boils at 131° and, when oxidised by Lieben's method, yields *iso*valeraldehyde boiling at 90—95°. Potassium hydroxide has no action on the aldehyde at the ordinary temperature, but, on careful addition of water so that the temperature is maintained at 20—25°, the aldehyde is converted into the aldol; if the temperature is allowed to rise above 30°, the unsaturated aldehyde, $C_{10}H_{18}O$, is formed.

The aldol, $CH_2Pr^{\beta}\cdot CH(OH)\cdot CHPr^{\beta}\cdot COH$, is formed also by the action of a saturated aqueous solution of potassium carbonate (4 weeks at 10°) on the aldehyde. It crystallises in delicate, white, glistening needles, melts at 83—84°, distils unchanged at 110° under 9 mm.

pressure, and, when distilled under atmospheric pressure, decomposes partially into the unsaturated aldehyde and water. When pure, the aldol is stable in air, but if traces of the unsaturated aldehyde are present, or if it is treated with an aqueous alkali hydroxide, or if it is placed over sulphuric acid in a vacuum, it decomposes to a liquid containing the unsaturated aldehyde and its acid. The oxime, $C_{10}H_{20}O\colon NOH$, is a viscid liquid which boils at 157° under 14 mm. pressure, and decomposes on repeated distillation. The aldol is not acted on by aluminium amalgam or by sodium amalgam in neutral solution; the action of sodium and sulphuric acid or of zinc and acetic acid leads to the formation of the unsaturated aldehyde and its reduction products. When warmed with silver oxide or potassium permanganate and water, the aldol yields traces of valeric acid and the acid, $CH_2Pr^{\beta}\cdot CH(OH)\cdot CHPr^{\beta}\cdot CO_2H$, which crystallises in white needles, melts at 81—82°, distils unchanged at 163° under 18 mm., or with partial decomposition into the unsaturated acid, at 240—244° under atmospheric pressure; the silver salt, $C_{10}H_{19}O_3Ag$, is crystalline.

The differences, as to the properties of the aldol, between the present results and the statements in the literature are due to previous authors having prepared the aldol from *iso*valeraldehyde obtained from impure *iso*amyl alcohol. G. Y.

The Condensation Product of Formyl*iso*butyraldol with Acetaldehyde. EDMUND WEIS (*Monatsh.*, 1904, **25**, 1065—1072). —The condensation product, $OH\cdot CH_2\cdot CMe_2\cdot CH(OH)\cdot CH_2\cdot COH$, obtained from acetaldehyde and formyl*iso*butyraldol, does not form an additive compound with bromine. The *oxime*, $C_7H_{15}O_3N$, forms a viscid, yellow oil having an odour of honey; the *diacetyl* derivative, $C_7H_{12}O(OAc)_2$, prepared by boiling the condensation product with acetic anhydride and sodium acetate, is a heavy, yellow oil, which has a pleasant odour and reduces ammoniacal silver solutions.

When reduced with aluminium amalgam in alcoholic solution, the dihydroxyaldehyde yields the *alcohol*, $C_7H_{13}(OH)_3$, which is a viscid, colourless oil, has a bitter flavour, and does not reduce ammoniacal silver solutions. G. Y.

Phosphorus Acid Derivatives of Ketones and Aldehydes. CHARLES MARIE (*Ann. Chim. Phys.*, 1904, [viii], **3**, 335—432).—The paper is mainly a *résumé* of work already published (compare Abstr., 1901, i, 635; 1902, i, 71, 255, 431, 714; 1903, i, 220, 328, 379, 678; 1904, i, 723, ii, 481), with the following corrections and additions: hydroxy*iso*propylhypophosphorous acid melts at 52° and not at 45°, its ethyl ester has n_D 1·452 at 18·5° and sp. gr. 1·122 at 22·5°; the ethyl ester of hydroxy*iso*propylphosphinic acid boils at 145° under 20 mm. pressure and melts at 14—15°; the acid, $COMePh,H_3PO_2$, obtained by the action of hypophosphorous acid on acetophenone, melts at 85° and not at 70°. Hydroxy*iso*valerylphosphinic acid, obtained either by the action of phosphorous acid on *iso*valeraldehyde or by oxidising the acid prepared from hypophosphorous acid and the aldehyde, melts at 191° and not at 182—184°, as stated by Fossek (compare Abstr.,

1884, 833); and the acid, $(C_5H_{11}O)_2,H_3PO_2$, obtained as a by-product in the above reaction melts at 230° and not at 160°, as stated by Ville (*Thèse*, Paris, 1890). Hydroxybenzylhypophosphorous acid, obtained by the action of benzaldehyde on hypophosphorous acid, melts at 108° and not at 90°, as stated by Ville, the *silver* salt is white; the *methyl* ester melts at 99°; and the *benzoyl* derivative at 93°. M. A. W.

A Compound of Mesityl Oxide with Mercuric Chloride. ERNST ERDMANN (*Ber.*, 1904, 37, 4571—4572. Compare Willstätter and Pummerer, Abstr., 1904, i, 1043).—Mesityl oxide forms a definite additive *compound*, $C_6H_{10}O,HgCl_2$, which is sparingly soluble in mercuric chloride solution. It crystallises from alcohol in colourless needles, has no definite melting point, but sublimes and decomposes when heated.

Methylheptenone $CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2Ac$, and cineol do not yield similar compounds, whereas cinnamaldehyde gives the *compound* $C_9H_8O,HgCl_2$. J. J. S.

Preparation of α-Substituted β-Ketonic Acids and of Ketones of the Aliphatic Series. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1904, iii, 31, 1153—1159. Compare Abstr., 1904, i, 847 and 848).—Ceresole showed (Abstr., 1882, 1052) that the lower members of the substituted acetoacetic esters are readily saponified by agitation with cold potassium hydroxide solution, but this method is inapplicable where the substituting group contains more than C_5. For the hydrolysis of the higher members of the series, the use of sulphuric acid is now recommended. The ester is rapidly poured into four or five times its weight of sulphuric acid previously heated at from 85—95°, and the mixture maintained at this temperature for a few minutes: it is then rapidly cooled and extracted with ether. From the latter, the β-ketonic acid is isolated by agitation with an aqueous solution of sodium carbonate. For the preparation of the ketones, it is unnecessary to isolate the acid first: it is sufficient to pour the sulphuric acid mixture into twice its bulk of water and then distil in a current of steam. A number of ketones were prepared by this process.

The *semicarbazone* of methyl butyl ketone crystallises in spangles from a mixture of light petroleum and alcohol and melts at 127° (corr), that of methyl hexyl ketone is similar and melts at 122—123° (corr.), the corresponding *derivative* of propyl *iso*butyl ketone crystallises in slender needles and melts at 124° (corr.). *Ethyl* n-*amyl ketone* is a mobile liquid with a fruity odour; it boils at 167—168° and yields a semicarbazone, crystallising in spangles and melting at 117—117·5° (corr.) (compare Abstr., 1903, i, 569). The *semicarbazone* of ethyl *iso*amyl ketone (Ponzio and de Gaspari, Abstr., 1899, i, 252) melts at 132—133° (corr.). *Propyl amyl ketone* is a colourless, mobile liquid, boils at 75—76° under 10 mm. pressure, and has a sp. gr. 0·837 at 0°/4°; the *semicarbazone* forms small, white lamellæ and melts at 73—74°.

Methyl β-methyloctyl ketone, $C_6H_{13}{\cdot}CHMe{\cdot}CH_2{\cdot}COMe$, is a mobile liquid with a slight odour of fat: it boils at 115° under 25 mm.

pressure; the *semicarbazone* separates from benzene in colourless crystals and melts at 66°. *Amyl β-methyloctyl ketone*,

$$C_6H_{13}\cdot CHMe\cdot CH_2\cdot CO\cdot C_5H_{11},$$

is a slightly viscous, colourless liquid with a fatty odour: it boils at 143—144° under 9 mm. pressure and has a sp. gr. 0·845 at 0°/4°.

T. A. H.

Preparation of α-Diketone Monoximes of the Type R·CO·CR'∶N·OH. Louis Bouveault and René Locquin (*Bull. Soc. chim.*, 1904, [iii], **31**, 1159—1164. Compare Abstr., 1904, i, 848).—The authors have generalised the process devised by Meyer and Züblin (Abstr., 1878, 487, 659), and improved by Ceresole (Abstr., 1882, 1052, 1883, 41), for the preparation of the monoximes of α-diketones by the action of nitrous acid on α-alkylacylacetic acids (compare Claisen and Manasse, Abstr., 1887, 944, and 1889, 584; Behr-Bregowski, Abstr., 1897, i, 459; and Ponzio, Abstr., 1897, i, 551).

Ceresole's process is used for the β-ketonic acids soluble in water (that is, members of the series below amylacetoacetic acid). For the acids of the series insoluble in water, it is best to use ether or chloroform as the solvent and nitrosyl chloride or nitrosylsulphuric acid as the generator of nitrous acid. The reaction is carried out at temperatures varying from 0° to 20°, and, when completed, the mixture is poured into a slight excess of sodium carbonate solution, the oxime being obtained by distilling off the solvent and rectifying the residue by distillation under reduced pressure. The yield is from 80 to 95 per cent. The method is, however, only applicable to acids below the term *sec*-octylhexoylacetic acid; the latter, when treated in this way, yields the corresponding ketone mixed with a small quantity of the diketone.

T. A. H.

Oximes and Dioximes of α-Diketones. René Locquin (*Bull. Soc. chim.*, 1904, [iii], **31**, 1164—1169. Compare preceding abstract).—Diacetylmonoxime semicarbazone melts with decomposition at 303° (corr.) on the mercury-bath or Maquenne block (compare Diels, Abstr., 1902, i, 205). Propionylbutyryloxime, $NOH\colon CEt\cdot COPr^{\alpha}$, which was not obtained pure owing to the presence of an impurity in the ethylbutyrylacetic acid used (Locquin, Abstr., 1904, i, 552), boils at 107—108° under 10 mm. pressure (Abstr., 1902, i, 659). *Dibutyryloxime*, prepared from ethyl propylbutyrylacetate, was not obtained pure; the preparation was liquid and boiled at 117—120° under 12 mm. pressure. *Butyryl*iso*butyryloxime*, $NOH\colon CPr^{\beta}\cdot COPr^{\alpha}$, obtained like the foregoing in an impure state, boiled at 115—119° under 14 mm. pressure. *Propionyl*iso*valeryloxime*, $NOH\colon CEt\cdot CO\cdot CH_2Pr^{\beta}$, melts at 38—39° and boils at 117—118° under 12 mm. pressure; the corresponding *dioxime* crystallises in translucent lamellæ from alcohol and melts and sublimes at 166—167° (corr.). Acetylhexoyloxime,

$$NOH\colon C(C_5H_{11})\cdot COMe,$$

melts at 54° and boils at 133° under 11 mm. pressure (compare Behr-Bregowski, Abstr., 1897, i, 459, and Ponzio and Prandi, Abstr., 1899,

i, 253); the dioxime melts at 173° (corr.) (compare Fileti and Ponzio, Abstr., 1895, i, 499). The isomeric acetylhexoyloxime,

$NOH:CMe\cdot CO\cdot C_5H_{11}$,

boils at 139° under 16 mm. pressure and melts at 39° (compare Ponzio and de Gaspari, Abstr., 1899, i, 252). *Propionylhexoyloxime*,

$NOH:CEt\cdot CO\cdot C_5H_{11}$,

forms brilliant, colourless needles, melts at 33—34°, boils at 131—132° under 9 mm. pressure, and is soluble in organic solvents; the corresponding *dioxime* crystallises from boiling benzene in needles and melts and sublimes at 158—158·5° (corr.). *Acetylnonoyloxime*,

$COMe\cdot C:NOH\cdot CHMe\cdot C_6H_{13}$,

boils at 147—149° under 10 mm. pressure, and has a sp. gr. 0·948 at 0°/4°; the corresponding *dioxime* is difficult to purify; the *semicarbazone* crystallises from light petroleum and melts at 178° (corr.).

T. A. H.

General Method for the Preparation of α-Diketones. Louis Bouveault and René Locquin (*Bull. Soc. chim.*, 1904, [iii], **31**, 1169—1172. Compare Abstr., 1904, i, 546, 556).—The authors recommend for this purpose the hydrolysis of the diketone monoximes prepared as already described (this vol., i, 19). Von Pechmann's method of hydrolysing these oximes is tedious (Abstr., 1888, 248), and the authors recommend instead the use of nitrous acid, which, as Claisen and Manasse have observed, when used in excess, converts the *iso*nitrosoketones into diketones. Nitrous anhydride, prepared by Lunge's method (Abstr., 1879, 200), is passed into the diketone-oxime for from one to two hours, the temperature being kept below 40°. The product, after being washed with a solution of sodium carbonate, is rectified under reduced pressure. Nitrosylsulphuric acid may also be employed in this reaction as a source of nitrous acid. T. A. H.

α-Diketones. René Locquin (*Bull. Soc. chim.*, 1904, [iii], **31**, 1173—1176. Compare preceding abstract).—The diketones reduce ammoniacal silver nitrate in the cold (compare Petrenko-Kritschenko and Eltschaninoff, Abstr., 1901, i, 506), and with the exception of the higher members readily combine with sodium hydrogen sulphite, even when they do not contain the group $CH_3\cdot CO\cdot$. The latter reaction permits of the ready separation of the diketones of the type

$CH_2R\cdot CO\cdot CO\cdot CH_2R'$,

where these do not contain more than twelve atoms of carbon, from the mono-ketones of the form $CH_2R\cdot CO\cdot CH_2\cdot CH_2R'$, which are not separable by fractional distillation.

Propionylbutyryl, $CH_2MeCO\cdot COPr^{\alpha}$, has an odour like that of diacetyl, boils at 145—146°, and has a sp. gr. 0·885 at 0°/4° (compare Ponzio and Borelli, Abstr., 1902, i, 659); the dioxime melts at 164—165° on the mercury-bath. Dibutyryl boils at 59—60° under 12 mm. pressure and at 166—169° under 755 mm. pressure, and has a sp. gr. 0·934 at 0°/4°; the dioxime crystallises in needles and melts and sublimes at 186—187° (corr.) on the mercury-bath (compare Ponzio, Abstr., 1901, i, 452). *Propionylisovaleryl*, $COEt\cdot CO\cdot CH_2Pr^{\beta}$, boils at 59—60° under 18 mm. pressure. *Propionylhexoyl*, $COEt\cdot CO\cdot C_5H_{11}$,

boils, after regeneration from its bisulphite compound, at 77—80° under 11 mm. pressure, and has a sp. gr. 0·927 at 0°/4°. *Acetylnonoyl*, $COMe\cdot CO\cdot CHMe\cdot C_5H_{11}$, is a mobile liquid with a fatty odour; it boils at 94° under 10 mm. pressure and has a sp. gr. 0·891 at 0°/4°.

T. A. H.

Reaction of Aldehydic Sugars. ARMAND BERG (*Bull. Soc. chim.*, 1904, [iii], **31**, 1216—1217).—From 0·02 to 0·03 gram of the sugar is added to 10 c.c. of freshly prepared saturated bromine water and warmed for 10 minutes at 60—70°; the bromine is then boiled off, and 10 c.c. of a reagent prepared by adding 4 drops of ferric chloride solution (45° B.) and 2 drops of hydrochloric acid to 100 c.c. of water added. Aldoses under these conditions give an intense yellow coloration, whereas ketoses give no coloration when pure. Commercial sucrose gives a slight yellow colour unless previously recrystallised from alcohol. In applying this reaction to bioses and more complex sugars, care must be taken that the bromine water is free from hydrobromic and other mineral acids. T. A. H.

A New Sugar from Mountain-Ash Berries. GABRIEL BERTRAND (*Compt. rend.*, 1904, **139**, 802—805. Compare Vincent and Meunier, Abstr., 1899, i, 185).—When the sorbite present in mountain-ash berries has been completely converted into sorbose by the action of the sorbose bacterium and the sugar removed by crystallisation, the mother liquor contains a hexahydric alcohol which can be separated in the form of an acetal by treating the syrup with benzaldehyde and sulphuric acid. The syrupy liquid obtained by concentrating the solution resulting from the hydrolysis of the acetal is treated with boiling absolute alcohol; after a time, the solution deposits crystals of the alcohol, *sorbieritol*. The statement of Vincent and Meunier that this alcohol contains eight atoms of carbon is refuted by the author's experiments. Sorbieritol melts at 75°, is exceedingly soluble in water, and deliquesces in moist air. Its aqueous solution is lævorotatory; $[\alpha]_D$ − 3·53° in 10 per cent. solution at 20°. The analysis of sorbieritol and the cryoscopic determination of its molecular weight correspond with the formula $C_6H_{14}O_6$. It yields a hexa-acetyl ester, crystallising from alcohol in hexagonal plates and melting at 123°. In 5 per cent. chloroform solution, $[\alpha]_D$ 26·66°. With benzaldehyde in presence of sulphuric acid, it gives a mixture of two acetals—a dibenzoic acetal readily soluble in boiling alcohol and melting at 192°, and a tribenzoic acetal much less soluble in alcohol and melting at 240°. H. M. D.

Synthesis and Chemical Nature of Sorbieritol. GABRIEL BERTRAND (*Compt. rend.*, 1904, **139**, 983—986).—The author finds that sorbieritol (compare preceding abstract) is identical in crystalline form, melting point, and specific rotation with *d*-iditol, prepared together with *d*-sorbitol by the reduction of sorbose in acid solution (compare Abstr., 1898, i, 550), and, further, the acetyl and tribenzoyl derivatives of the two alcohols have the same physical constants. By

taking advantage of the selective oxidising property of the sorbose bacterium (compare Abstr., 1898, 559), it is possible to separate *d*-iditol or synthetical sorbieritol from its isomeride, *d*-sorbitol, in the mixture of the two alcohols obtained by reducing sorbose. The original contains the constitutional formulæ of sorbose, *d*-sorbitol, and *d*-iditol or sorbieritol (compare Fischer and Fay, Abstr., 1895, i, 650).
M. A. W.

Hydrolysis of Sucrose by *d*- and *l*-Camphor-β-sulphonic Acids. Robert J. Caldwell (*Proc. Roy. Soc.*, 1904, **74**, 184—187).—So far as the inversion of sucrose is concerned, no difference in the activity of the *d*- and *l*-acids can be detected. The activity of camphor-β-sulphonic acid, as deduced from the sucrose experiments, stands to that of hydrochloric acid in the ratio 89·8 : 100. When the hydrolysis of milk sugar is made the basis of comparison, the value of the ratio is found to be 70 : 100.
J. C. P.

***iso*Maltose.** Hermann Ost (*Zeit. angew. Chem.*, 1904, **17**, 1663—1670. Compare Grüters, Abstr., 1904, i, 852).—Further evidence is submitted to prove that the *iso*maltose, supposed by Lintner and Düll to be formed as an intermediate product between dextrins and maltose during the hydrolysis of starch, does not exist. E. Fischer's *iso*maltose, formed during the inversion of dextrose by acids, is not identical with Lintner and Düll's product.

In addition to dextrose and dextrins, a considerable amount of maltose was formed as an intermediate product during the hydrolysis of starch by oxalic acid. Lintner and Düll's *iso*maltose, with $[\alpha]_D + 140°$ and a reducing power 80—84 per cent., consists of a mixture of maltose, easily soluble dextrins, and substances which are not sugars. A suitable method of distinguishing between maltose and Fischer's *iso*maltose, which is not fermentable by yeast, is given by the rotation of the corresponding osazones. Maltosazone is strongly dextrorotatory, and the value of its rotation is increased when dextrins are present; Fischer's *iso*maltosazone is lævorotatory.
A. McK.

Constitution of Cellulose. II. Arthur G. Green (*Zeit. Farb. Text.-Ind.*, 1904, **3**, 309—310).—A reply to criticisms by Cross and Bevan (Abstr., 1904, i, 652) of a previous paper (*Zeit. Farb. Text.-Ind.*, **3**, 97) in which the formula

$$\begin{array}{l} CH(OH)\cdot CH\cdot CH(OH) \diagdown \\ | \qquad\qquad\qquad > O \qquad\qquad > O \\ CH(OH)\cdot CH\text{———}CH_2 \diagup \end{array}$$

for cellulose was suggested. The determination of the number of acetyl groups in Cross and Bevan's "tetra-acetylcellulose" gave values more closely in agreement with the assumption that this substance is a triacetylcellulose.
W. A. D.

Lignin. Viktor Grafe (*Monatsh.*, 1904, **25**, 987—1029).—Lignin consists principally of vanillin, methylfurfuraldehyde, catechol, and coniferin in ethereal combination with cellulose. On hydrolysis of the cellulose ethers with dilute acids or alkali hydroxides, furfuraldehyde is formed from the pentoses of the wood; this is avoided by hydrolysis

with water at 180° in a vacuum, or by electrolysis in warm water under pressure. Vanillin is found also in the sulphite mother liquors obtained in the commercial preparation of cellulose.

Wiesner's and Mäule's reactions take place with the phenolic components of lignin, and, as methylfurfuraldehyde and catechol can be formed simply from cellulose, cannot be used as tests for its presence. The blue coloration obtained by the action of phenol, hydrochloric acid, and potassium chlorate on wood is to be ascribed to the presence of coniferin, and the green coloration with hydrochloric or hydrobromic acid to methylfurfuraldehyde in combination with coniferin. The intensity of the colour reactions of wood is due to the sensitiveness of the phenol dyes, to the finely divided state in which these are distributed through the substance, and to the manner in which cellulose retains substances which have permeated it.

Methoxyl determinations show lignin to contain 48 per cent. of vanillin if that is the only methoxy-compound present. Vanillin, methylfurfuraldehyde, and catechol constitute the so-called hadromal, the chromogen of lignin. G. Y.

Choline, Neurine, and Allied Compounds. ERNST A. SCHMIDT (*Annalen*, 1904, **337**, 37—121. Compare Abstr., 1892, 905).—A study has been made of the derivatives of choline, neurine, and muscarine, mainly with the object of ascertaining the variation of physiological action with change of constitution.

In the case of neurine, addition of alkyl groups not only weakens the physiological action, but also alters its character; it is remarkable, however, that trimethylneurine is more active than the dimethyl derivative.

Natural muscarine ("pilzmuscarin"), when compared with the artificial muscarines, cholinemuscarine, or ψ-muscarine from Prussian blue, is physiologically inactive. On comparing the behaviour of homo*iso*muscarine with that of *iso*muscarine, it was found, as in the case of the neurines, that lengthening of the side-chain reduces the physiological activity.

When choline is converted into the ethyl or methyl ether, $OH{\cdot}NMe_3{\cdot}CH_2{\cdot}CH_2{\cdot}OEt$, it is found that the toxic action was markedly increased.

[With WALDEMAR WAGNER.]—Bromine only attacks choline when they are heated together under pressure at 120—130°; the product, a perbromide, is converted by boiling with alcohol into trimethylbromoethylammonium bromide, $C_2H_4Br{\cdot}NMe_3Br$, which forms colourless crystals melting at 230°; the *platinichloride*, $(C_2H_4Br{\cdot}NMe_3)_2PtCl_6$, prepared by decomposing the bromide with silver chloride and adding platinic chloride, forms octahedral crystals melting at 240°. The *aurichloride* forms prismatic crystals melting at 222—223°. On treatment with moist silver oxide, the bromide is converted into neurine.

Choline chloride is only attacked by sulphuric acid at 100°, a sulphate being obtained which is identical with that formed on treating trimethylbromoethylammonium bromide with silver sulphate; it has therefore the formula $CH_2{<}\begin{matrix}CH_2-SO_3\\ \quad\ \ \vert \\ NMe_3{\cdot}O\end{matrix}$; it crystallises in white

leaflets and decomposes without melting. No dehydration with the production of neurine appeared to occur.

Attempts to convert choline into neurine by the action of phosphorus oxychloride or zinc chloride failed; the substance first mentioned led to the production of a salt which yielded the *platinichloride*, $(C_2H_4Cl\cdot NMe_3Cl)_2PtCl_4$, a compound crystallising in octahedra and not melting at 250°; the *aurichloride* crystallises in needles melting at 239°.

Choline is converted by nitric acid into nitrosocholine, the *platinichloride* of which, $(NO\cdot O_2\cdot C_2H_4\cdot NMe_3)_2PtCl_6$, is anhydrous and does not crystallise with $2H_2O$, as Nothnagel states (*Arch. Pharm.*, 1904, 284). The *aurichloride* crystallises in groups of needles melting at 234° The formation of cholinemuscarine was not observed.

The ethers of choline are not produced either by the action of methyl iodide and sodium methoxide on choline chloride or by the action of sodium methoxide on trimethylbromoethylammonium bromide, but can be easily obtained by the action of methyl bromoethyl ether or bromoethyl ether on trimethylamine. The *iodide* of choline methyl ether, $OMe\cdot CH_2\cdot CH_2\cdot NMe_3I$, is prepared from iodoethyl methyl ether and 33 per cent. trimethylamine, and crystallises in hygroscopic needles. The *platinichloride* crystallises in yellowish-red needles melting at 216—217°, and the *aurichloride* in yellow needles melting at 156°. The corresponding *bromide*, prepared in a similar manner, crystallises in hygroscopic needles; it was converted into the corresponding *chloride*, which yielded with excess of mercuric chloride the double *salt*, $C_2H_4(OH)\cdot NMe_3Cl,6HgCl_2$; the latter forms crystals melting at 205°.

The corresponding ethyl ether of choline, $OEt\cdot C_2H_4\cdot NMe_3Br$, is prepared from bromoethyl ether and trimethylamine, and forms crystals melting at 175°. The *platinichloride* forms reddish-yellow prisms melting at 243°, and the *aurichloride* needles or leaflets melting at 140°.

Bromoethyl ether combines with pyridine in a similar manner, yielding the *compound* $OEt\cdot C_2H_4\cdot C_5NH_5Cl$, which could not be isolated, but which was converted into an *aurichloride*, crystallising in small needles.

[With Waldemar Wagner.]—An attempt was made to convert neurine into choline by the addition of the elements of water effected by repeated evaporation of the nitrate with dilute nitric acid; very little of the neurine was changed, but traces of choline and nitrosocholine were found in the product.

Neurine combines with sulphurous acid forming *taurobetaine*,

$$CH_2<\begin{matrix}CH_2-SO_3\\ \qquad\ \ |\\ NMe_3\cdot O\end{matrix},$$

which forms crystals insoluble in alcohol and not molten at 250°.

Attempts to convert neurine into *iso*muscarine by oxidation with 1 per cent. permanganate in neutral solution did not give the desired result; the neurine was mainly unchanged, a small quantity of trimethylamine being also formed. Treatment of neurine dibromide with silver nitrate with the object of obtaining *iso*muscarine led only to the production of a small quantity of *trimethylbromovinylammonium chloride*, $CHCl\!:\!CH\cdot NMe_3Cl$, the *platinichloride* of which

crystallised in leaflets melting at 201°, and the *aurichloride* in yellow prisms melting at 210°.

Neurine was not reduced either by zinc and sulphuric acid or by sodium amalgam.

[With FRANZ M. LITTERSCHEID.]—The action of methylene iodide on trimethylamine, by which Hofmann prepared trimethyliodomethylammonium salts, depends greatly on the conditions. At a low temperature, trimethyliodomethylammonium salts are formed; the *platinichloride* crystallises in needles or leaflets, becoming brown at 215° and melting and decomposing at 235°, and the *aurichloride* in yellow needles melting at 249°, and the *mercurichloride* in needles melting at 174—175°. The *base* is a crystalline, hygroscopic mass, and the chloride forms hygroscopic plates melting at 178—179°, and the *picrate* long, yellow needles melting at 196°. When trimethylamine and the iodide are heated under pressure for 1 hour, the same products are obtained as at the ordinary temperature. After 2 hours' heating, tetramethylammonium salts are also formed, the *aurichloride* crystallising in needles not melting at 250°. After 4 hours' heating, the tetramethylammonium iodide is the only solid, the liquid containing, besides formaldehyde, the iodide of a *base* melting at 207—208°, the aurichloride of which melts at 140°. When trimethyliodomethylammonium iodide is heated with trimethylamine under pressure, the same products are obtained, showing that on heating methylene iodide with trimethylamine, the base, trimethyliodomethylamine, first formed reacts with the excess of trimethylamine. Ammonia does not react with trimethyliodomethylammonium iodide.

Trimethylbromomethylammonium bromide, $CH_2Br\cdot NMe_3Br$, prepared from trimethylamine and methylene bromide, forms large, flat crystals melting at 160°; the *platinichloride*, $(CH_2Br\cdot NMe_3Br)_2PtCl_4$, forms red, octahedral crystals blackening and melting at 208°, whilst the *platinichloride*, $(CH_2Br\cdot NMe_3)_2PtCl_6$, forms yellow, octahedral crystals melting at 199°. The base forms a hygroscopic, crystalline mass, which is converted into the carbonate when exposed to the air.

[With FRANZ M. LITTERSCHEID.]—Formocholine (*trimethylhydroxymethylammonium hydroxide*), $OH\cdot CH_2\cdot NMe_3\cdot OH$, forms a crystalline, hygroscopic mass; the *platinichloride* crystallises in readily soluble octahedra melting and decomposing at 230°, and the *aurichloride* in slender, yellow needles, which do not melt at 250°. The *mercurichloride* forms plates not melting at 250°. Attempts to acetylate and benzoylate formocholine by heating the chloride with acetyl chloride or benzoyl chloride only lead to the formation of tetramethylammonium salts. Attempts to prepare formocholine by heating trimethylbromomethylammonium bromide with water under pressure only resulted in complex decomposition.

[With WALDEMAR WAGNER.]—On reducing trimethylbromoethylammonium bromide either with sodium amalgam or zinc and sulphuric acid, trimethylamine is formed.

When the bromide is heated with a solution of silver sulphate for 2 days, the *compound*, $CH_2<\begin{matrix}CH_2-SO_3\\ NMe_3\cdot O\end{matrix}$, is obtained as a white, crystal-

line powder or leaflets, which give no precipitate with barium until boiled with hydrochloric acid. In this reaction, a small portion of trimethylbromoethylammonium salts and choline are produced.

When trimethylbromoethylammonium bromide is boiled with alcoholic silver nitrate, no choline is produced, but the compound

$$NO_3\cdot CH_2\cdot CH_2\cdot NMe_3\cdot NO_3.$$

From it a *platinichloride*, $(NO_3\cdot CH_2\cdot CH_2\cdot NMe_3)_2PtCl_6$, is obtained in reddish-yellow, soluble crystals melting at 227—228°; the *aurichloride* forms soluble needles melting at 133°.

[With G. Kleine.]—Ethylene bromide and trimethylamine react together at the ordinary temperature, giving trimethylbromoethylammonium bromide, but, when heated together under pressure at 100°, there are also produced tetramethylammonium bromide, hexamethylethylenediamine bromide, neurine bromide, trimethylamine hydrobromide, and dimethylamine hydrobromide, together with aldehyde and aldehyde resin. The *platinichloride* of hexamethylethylenediamine, $C_2H_4(NMe_3)_2PtCl_6$, crystallises in small, pale orange plates, becoming black at 260° and melting at 275—276°; the *aurichloride* crystallises in golden-yellow leaflets melting at 223—225°.

When propylene bromide and trimethylamine were heated together for 6 hours at 100° in alcoholic solution, α-bromopropylene, trimethylamine, and dimethylamine hydrobromide and trimethylpropenylammonium bromide, $C_3H_5\cdot NMe_3Br$, are formed. The *platinichloride* of the propenyl derivative, $(C_3H_5\cdot NMe_3)_2PtCl_6$, crystallises in dark orange-red scales melting and decomposing at 249°; the *aurichloride* forms yellow needles melting at 199—202°.

*iso*Butylene bromide reacts with trimethylamine in alcoholic solution both at the ordinary temperature and at 100° with the production of *iso*crotyl bromide and trimethylamine hydrobromide. The *iso*crotyl bromide combines to a small extent with trimethylamine, forming *trimethyl*isocrotyl*ammonium bromide*, which was isolated as a *platinichloride*, $(C_4H_7\cdot NMe_3)_2PtCl_6,H_2O$, which crystallises in long, orange leaflets melting at 206—207°; the *aurichloride* forms large, golden-yellow needles melting at 190—191°. Experiment showed that *iso*crotyl bromide would not combine directly with trimethylamine. The *perbromide* of trimethyldibromo*iso*butylammonium bromide,

$$C_4H_7Br_2\cdot NMe_3Br,Br_2,$$

is obtained in reddish-brown crystals when the *iso*crotyl salt is treated with bromine in chloroform solution; on boiling with alcohol, it is converted into *trimethyldibromo*iso*butylammonium bromide*, which crystallises in leaflets melting at 145°. The *platinichloride*,

$$(C_4H_7Br_2\cdot NMe_3)_2PtCl_6,$$

crystallises in orange-red scales melting at 212—213°. The *aurichloride* forms needles melting at 145°. When treated with moist silver oxide, *trimethylbromo*iso*crotylammonium hydroxide* is produced, and yields the *platinichloride*, $(C_4H_7Br_2\cdot NMe_3Cl)_2PtCl_4$, which forms orange, star-shaped groups of needles melting at 203—204°, and an *aurichloride* which crystallises in lemon-yellow needles melting at 126°.

ψ-Butylene bromide interacts with trimethylamine in alcoholic solution both at the ordinary temperature and at 100°, yielding trimethylamine hydrobromide, ψ-crotyl bromide, the bromide of hexamethyl-ψ-

butylenediamine; the *platinichloride*, $C_4H_8(NMe_3)_2PtCl_6$, forms crystals melting at 221—222°. On attempting to form the aurichloride, a decomposition took place, the *aurichlorides* of trimethyl-ψ-crotylammonium chloride, $C_3H_7\cdot NMe_3,AuCl_4$, a substance melting at 175°, and of trimethylamine hydrochloride were obtained.

Amylene bromide and trimethylamine were brought together in alcoholic solution and heated at 100°; the main product is *trimethylpentenylammonium bromide*, the *platinichloride* obtained from which crystallises with H_2O, and the *aurichloride* in small needles melting at 193°. At the same time, a small amount of *hexamethylamylenediammonium bromide* is produced; the *platinichloride*, $C_5H_{10}\cdot(NMe_3)_2PtCl_6$, crystallises in needles melting at 203°; it could not be converted into a gold salt, as trimethylamine is eliminated and valeryltrimethylammonium chloride produced. *Trimethylpentenylammonium bromide* readily forms the *perbromide*, $C_5H_9Br_2\cdot NMe_3Br,Br_8$, which is decomposed by alcohol.

[With Hilderich Hartmann.]—Trimethylglycerylammonium chloride, prepared by Meyer and Scholten's method from α-monochlorhydrin and trimethylamine, yields a dibenzoate when heated with benzoic anhydride; the *platinichloride*, $[C_3H_5(OBz)_2\cdot NMe_3]_2PtCl_6$, is a red solid melting at 191°. The glyceryl-ammonium salt is converted by red phosphorus and hydriodic acid into the compound $C_3H_5I_2\cdot NMe_3I$, which forms leaflets; in the mother liquor, another base is contained, and can be isolated as an *aurichloride*, $OH\cdot C_3H_5I\cdot NMe_3,AuCl_4$, crystallising in yellow leaflets melting at 101°; the *platinichloride* crystallises in reddish-brown needles, becoming black at 176° and melting and decomposing at 194°.

When oxidised with nitric acid, a compound is formed which can be isolated as *platinichloride*, $[CO_2H\cdot CH(OH)\cdot CH_2\cdot NMe_3]_2PtCl_6$, crystallising in yellowish-red tetrahedra melting at 233°; the *aurichloride* forms lemon-yellow crystals melting at 172°. It is suggested that this compound is possibly not a hydroxyhomobetaine, but a hydroxyhomomuscarine, $CH(OH)_2\cdot CH(OH)\cdot CH_2\cdot NMe_3Cl$.

As regards the interaction of α-dichlorohydrin and trimethylamine, the results of other observers are confirmed.

β-Dibromohydrin and trimethylamine react either at the ordinary temperature or at 100° with the elimination of hydrobromic acid; at the same time, hexamethylhydroxypropylenediammonium bromide is formed and isolated as *platinichloride*, $OH\cdot C_3H_5(NMe_3)_2,PtCl_6$, which crystallises in needles blackening at 256° and melting and decomposing at 263°; the *aurichloride* is a yellow, crystalline precipitate melting at 242—244°.

β-Dichlorohydrin behaves with trimethylamine as does the bromohydrin.

Allyl tribromide and trimethylamine are found to react in the manner described by Partheil (Abstr., 1890, 356), trimethylbromoallyl ammonium bromide and trimethylamine hydrobromide being formed.

Epichlorohydrin and trimethylamine readily react in the cold; on heating the mixture for six hours under pressure, trimethylhydroxypropylammonium bromide is the main product, the direct additive product of epichlorohydrin and trimethylamine being at the same time

produced; it was found to be identical with Partheil's anhydrohomo-*iso*muscarine (*loc. cit.*). K. J. P. O.

Hydrazinecarboxylic Acid. Robert Stollé and K. Hofmann (*Ber.*, 1904, **37**, 4523—4524).—On passing a current of carbon dioxide into a well-cooled concentrated aqueous solution of hydrazine, *hydrazinecarboxylic acid*, $NH_2\cdot NH\cdot CO_2H$, separates as a white powder, which may be dried over sulphuric acid in an atmosphere of carbon dioxide. It partially decomposes at 90° into carbon dioxide and *hydrazine hydrazinecarboxylate*, $NH_2\cdot NH\cdot CO_2H,N_2H_4$, which distils at 140° under the ordinary pressure, or at 75° under 23 mm. pressure as a clear, viscous liquid, slowly solidifying to a crystalline mass when kept over sulphuric acid, and then melting at about 70°. It dissolves very readily in water to an alkaline solution, but is rapidly decomposed by acids, and is partially decomposed to carbohydrazide on heating at 140° in a closed tube. With ethyl chlorosulphonate it yields *hydrazinedisulphonic acid*, which may be isolated in the form of its *potassium* salt,

$$N_2H_2(SO_3K)_2,H_2O,$$

crystallising from water in transparent prisms. The acid yields no condensation product with benzaldehyde.

Hydrazinemonosulphonic acid is also formed in the above reaction, and may be isolated in the form of potassium benzylidenehydrazinesulphonate.

Hydrazinecarboxylic acid and its hydrazine salt may be employed in many reactions in place of anhydrous hydrazine. The latter may also be prepared from them by distillation with calcium or barium oxide. An accidental explosion once occurred during the final distillation. C. H. D.

Some Substances of Physiological Importance. Martin Schenck (*Zeit. physiol. Chem.*, 1904, **43**, 72—73).—*Guanidine cadmium chloride*, $CH_5N_3,HCl,2CdCl_2$, obtained in the form of a voluminous precipitate by mixing concentrated alcoholic solutions of guanidine chloride and cadmium chloride, melts at 390—395°.

Biuret cadmium chloride, $(C_2H_5O_2N_3)_2,CdCl_2$, melts and decomposes at 255—260° and is only sparingly soluble in hot ethyl alcohol.

Histidine cadmium chloride, $C_6H_9O_2N_3,HCl,CdCl_2$, melts and decomposes at 270—275° and is practically insoluble in hot ethyl alcohol. All three compounds are readily soluble in water.

A compound of *arginine*, $(C_6H_{14}O_2N_4)_2,Cu(NO_3)_2,2H_2O$, melting at 226°, has also been prepared. J. J. S.

Diaminoguanidine. Robert Stollé and K. Hofmann (*Ber.*, 1904, **37**, 4524—4525. Compare Abstr., 1904, i, 980).—Anhydrous hydrazine reacts with cyanogen chloride in cooled ethereal solution to form *diaminoguanidine hydrochloride*, CH_7N_5,HCl, a white powder melting at 174°, and dissolving readily in water to a neutral solution which reduces ammoniacal silver nitrate. Cyanohydrazine is first formed, which then combines with a second molecule of hydrazine.

Diaminoguanidine hydrochloride reacts with benzaldehyde to form *dibenzylidenediaminoguanidine hydrochloride*, $C_{15}H_{15}N_5,HCl$, crystal-

lising from alcohol in pale yellow needles melting at 232°. The *base* crystallises from alcohol in yellow needles melting at 176°, insoluble in water, readily soluble in ether. C. H. D.

β-Alanine. F. H. Holm (*Arch. Pharm.*, 1904, **242**, 590—612).—Various methods for the preparation of β-alanine,

$$NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H,$$

have been examined. The conclusion drawn is that this substance is best prepared by the action of alkaline potassium hypobromite on succinimide (Hoogewerff and van Dorp, Abstr., 1891, 1216), as this method is the quickest, and at once gives a pure product; the yield is 60 per cent. of the theoretical.

β-Alanine melts at 196°; when heated for some time at this temperature, it decomposes for the most part into ammonia and acrylic acid. The *hydrobromide* melts at 105—115°, the *hydriodide* at 199°, the *aurichloride* at 144—145°, the *platinichloride* at 210°; the copper salt, with $6H_2O$, and *silver* salt, melting at 130°, were analysed. The *aurichloride* of the *ethyl* ester, melting at 143—146°, and *platinichloride* and *aurichloride* of the *methyl* ester, the former melting at 192°, the latter very deliquescent, were prepared for the first time. The *benzoyl* derivative melts at 120° and forms a *silver* salt which melts at 240°. C. F. B.

β-Alacreatine (β-Guanidopropionic Acid). F. H. Holm (*Arch. Pharm.*, 1904, **242**, 612—619).—This substance,

$$NH{:}C(NH_2){\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H,$$

was prepared from cyanamide and β-alanine (Mulder, this Journal, 1877, ii, 311). The hydrochloride, melting at 140°, is anhydrous; the *platinichloride* and *aurichloride* melt at 184° and 130—133° respectively.

When β-alacreatine is heated with fuming hydrochloric acid at 125—130° for 8 hours in a sealed tube, the *hydrochloride* of *β-alacreatinine*, $NH{:}C{<}{\substack{NH{\cdot}CH_2\\ NH{-}CO}}{>}CH_2$, is formed; this melts at 268—271°, the *platinichloride* at 220°, the *aurichloride* at 202°. When a solution of the hydrochloride is digested with lead oxide and the liquid freed from lead by means of hydrogen sulphide, the filtrate has a strong alkaline reaction at first, but this soon disappears, and β-alacreatine crystallises out; evidently β-alacreatinine itself is a very unstable substance, and rapidly takes up water, forming β-alacreatine. C. F. B.

Glycocyamine and Glycocyamidine. Georg Korndörfer (*Arch. Pharm.*, 1904, **242**, 620—640).—The glycocyamine (guanineacetic acid), $NH{:}C(NH_2){\cdot}NH{\cdot}CH_2{\cdot}CO_2H$, obtained from guanidine carbonate and glycine, is identical with that from cyanamide and glycine; the former method of preparation is the more convenient. The platinichloride crystallises with $2H_2O$; an *aurichloride*, melting at 173°, with the anomalous composition $2C_3H_7O_2N_3,HAuCl_4$ was obtained; the copper salt is only obtained constant in composition by precipitating a hot copper solution with a cold solution of glycocyamine and heating

the precipitate for half an hour at 100°. The solubility of glycocyamine in water is variable, but is apparently about 1 part in 230. When boiled with aqueous barium hydroxide, glycocyamine is hydrolysed to ammonia, carbon dioxide, glycine (a *sulphate* of which, containing 11·7 per cent. of SO_3, was obtained), and hydantoic acid (which melts at 171—173°).

Glycocyamidine, $NH{:}C{<}\begin{matrix}NH\cdot CH_2\\ |\\ NH\cdot CO\end{matrix}$, is best obtained by heating glycocyamine at 160—170° (at a slightly higher temperature, further decomposition occurs). Instead of the normal aurichloride, a *compound*, $C_3H_5ON_3,AuCl_3$, was obtained; the *monosilver* derivative was also analysed. When glycocyamidine is heated with methyl iodide in methyl-alcoholic solution at 100°, it is converted into a *methiodide* which does not melt below 245°; the *methochloride* also is unmelted at 245°, and so is the *platinichloride*, which crystallises with $2H_2O$; the *aurichloride* melts at 168°, the *picrate* at 193°, decomposition beginning at 180°. These salts are not identical with those of creatinine having the same composition (*creatinine hydriodide* melts at 194—195°). As they are hydrolysed by aqueous barium hydroxide to ammonia, methylamine, glycine, and hydantoic acid, they must be regarded as salts of *δ-methylglycocyamidine*, $NMe{:}C{<}\begin{matrix}NH\cdot CH_2\\ |\\ NH\cdot CO\end{matrix}$. When the iodide is treated with silver hydroxide, an alkaline solution is obtained at first, but this gradually becomes feebly acid, and it is then methylglycocyamine, not methylglycocyamidine, that is present in the solution. C. F. B.

Synthesis of Polypeptides. VII. Derivatives of Cystine. Emil Fischer and Umetaro Suzuki (*Ber.*, 1904, **37**, 4575—4581. Compare Abstr., 1903, i, 465, 607, 799; this vol., i, 652, 771, 867, 890).—Cystine combines with two molecules of acid chlorides containing halogen in alkaline solution forming crystalline products, which, when acted on by ammonia, are converted into the corresponding polypeptide derivatives. *Dichloroacetylcystine*, prepared from cystine and chloroacetyl chloride, crystallises in microscopic, colourless prisms or plates, melting to a colourless oil at 134·5—136·5° (corr.). *Diglycylcystine*, $S_2[CH_2\cdot CH(CO_2H)\cdot NH\cdot CO\cdot CH_2\cdot NH_2]_2$, separates as a colourless, transparent, amorphous mass, which dissolves copper oxide with a blue coloration. *Dibromopropionylcystine*, prepared by the interaction of cystine and bromopropionyl bromide, crystallises from a mixture of ethyl acetate and ether in long needles which sinter at 60°. The dry substance melts at 145·5—146·5° (corr.) to a brown oil and subsequently decomposes. *Dialanylcystine*, $S_2[CH_2\cdot CH(CO_2H)\cdot NH\cdot CO\cdot CHMe\cdot NH_2]$, forms stellate aggregates of microscopic prisms, which become coloured at 215° and decompose on further heating. In normal hydrochloric acid, it has $[\alpha]_D$ −192·8° at 20°. *Di-α-bromo*iso*hexoylcystine*, prepared from α-bromo*iso*hexoyl chloride and cystine, crystallises in microscopic, glistening, colourless prisms; these begin to sinter at 120° and gradually melt to an oil at 135°, which subsequently decomposes. *Dileucylcystine*,

$$S_2[CH_2\cdot CH(CO_2H)\cdot NH\cdot CO\cdot CH(C_4H_9)\cdot NH_2]_2,$$

is an amorphous substance sintering at 178°.

Inasmuch as cystine is stereochemically similar to active tartaric acid, three isomeric optically active products can be formed with a racemic acid chloride, which can be represented as *dd*, *ll*, and *dl*. In general, the combinations *dd*, *ll* will be formed in equal amounts, but the amount of the combination *dl* is independent of the amount of these and it may even be the sole product. In the case of dibromopropionylcystine, the product appears to be homogeneous and to represent, therefore, the *dl* form. E. F. A.

Synthesis of Polypeptides. VIII. Chlorides and Amides of Aspartic Acid. Emil Fischer and Ernst Koenigs (*Ber.*, 1904, **37**, 4585—4603).—*Chloroacetylasparagine*, prepared by the condensation of *l*-asparagine with chloroacetyl chloride in presence of sodium hydroxide, crystallises in needles melting at 148—149° (corr.) and is converted on heating with ammonia into *glycylasparagine*,

$$NH_2\cdot CH_2\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot CO\cdot NH_2,$$

which crystallises in needles, melting and decomposing at 216° (corr.) and has $[\alpha]_D - 6\cdot4°$ at 20°. *Ethyl chloroacetylaspartate*, prepared by treating ethyl *l*-aspartate with chloroacetyl chloride in presence of sodium carbonate, crystallises in long needles melting at 46—47°; heating with strong alcoholic ammonia converts it into *anhydroglycylasparagine*, probably $CH_2<\substack{CO\cdot NH \\ NH\cdot CO}>CH\cdot CH_2\cdot CO\cdot NH_2$, which crystallises in needles, and on heating turns brown at 245° (corr.) and decomposes at 274° (corr.). *Ethyl anhydroglycylaspartate*, crystallises in well formed leaflets melting at 211—212° (corr.).

*α-Bromo*iso*hexoylasparagine* is formed as a mixture of two isomerides from *l*-asparagine and *α-bromo*iso*hexoyl chloride*. These are separable by fractional crystallisation from water, the sparingly soluble portion crystallising in long, narrow prisms melting at 178° (corr.) and having $[\alpha]_D - 25\cdot6°$ at 20°, whilst the more soluble isomeride melts at about 148° (corr.) and has $[\alpha]_D + 15\cdot4°$. *Leucylasparagine*,

$$CH_2Pr^{\beta}\cdot CH(NH_2)\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot CO\cdot NH_2,$$

prepared by the action of aqueous ammonia on this mixture of isomerides, crystallises with $2H_2O$ in flat prisms melting at 195° (corr.), the anhydrous form melting and decomposing at 230° (corr.). *Ethyl α-bromo*iso*hexoylaspartate* crystallises in long, fine leaflets melting at 61—62° (corr.); the corresponding acid separates in colourless, crystalline aggregates which melt at 152—154° (corr.). *Leucylaspartic acid*, $CH_2Pr^{\beta}\cdot CH(NH_2)\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$, formed from the foregoing by the prolonged action of aqueous ammonia, crystallises with $1H_2O$ and melts and decomposes at 180—182° (corr.). *Diethyl fumaryldiglycine*, prepared by condensing fumaryl chloride with ethyl glycine in cold ethereal solution, melts at 211° (corr.); on hydrolysis with sodium hydroxide, it yields *fumaryldiglycine*,

$$C_2H_2(CO\cdot NH\cdot CH_2\cdot CO_2H)_2,$$

crystallising in colourless, oblique, four-sided plates melting and decomposing at 290° (corr.). On heating with aqueous ammonia for four hours under pressure at 100°, inactive *asparagylmonoglycine* is formed. This separates from water in tiny crystals and melts at 148° (corr.); boiling with hydrochloric acid converts it into glycine and *i*-aspartic

acid. *Diethyl fumaryldialanine* melts at 203—205° (corr.); *fumaryl-alanine* separates in microscopic rhombs melting and decomposing at 275° (corr.). *Aspartyldialanine*,

$$CO_2H\cdot CHMe\cdot NH\cdot CO\cdot CH_2\cdot CH(NH_2)\cdot CO\cdot NH\cdot CHMe\cdot CO_2H,$$

prepared by the action of ammonia on fumaryldialanine, crystallises with $2H_2O$ and melts at 115° (corr.), solidifies to a mass of fine leaflets and melts again at 150° (corr.).

Ethyl fumaryldiaspartate, prepared by the interaction of fumaryl-chloride with much ethyl aspartate, melts at 195°. *Chlorosuccinyl-dialanine*, $CO_2H\cdot CHMe\cdot NH\cdot CO\cdot CH_2\cdot CHCl\cdot CO\cdot NH\cdot CHMe\cdot CO_2H$, prepared from alanine and chlorosuccinyl chloride, crystallises in long prisms melting and decomposing at 210° (corr.).

Diethyl aspartate is conveniently prepared by the action of hot alcohol saturated with dry hydrogen chloride on asparagine. When exposed to the action of anhydrous liquid ammonia, it is converted into a mixture of aspartic diamide and asparaginimide. *Aspartic diamide*, $NH_2\cdot CO\cdot CH_2\cdot CH(NH_2)\cdot CO\cdot NH_2$, melts at 131°, reacts strongly alkaline, and gives a brilliant biuret coloration; characteristic salts could not be prepared. In methyl-alcoholic solution it has $[\alpha]_D$ about $-7°$.

Ethyl 2 : 5-*diketopiperazine*-3 : 6-*diacetate*,

$$CO_2Et\cdot CH_2.CH{<}{}^{NH\cdot CO}_{CO\cdot NH}{>}CH\cdot CH_2\cdot CO_2Et,$$

is best prepared by boiling ethyl aspartate in presence of a small quantity of zinc chloride for 48 hours: it crystallises in colourless needles melting at 179—180° (corr.). The ester is hydrolysed by dilute barium hydroxide and the solution gives a precipitate with silver nitrate, probably the *silver* salt of the acid. This ester is converted by liquid anhydrous ammonia into *diketopiperazinediacetamide*,

$$NH_2\cdot CO\cdot CH_2\cdot CH{<}{}^{CO\cdot NH}_{NH\cdot CO}{>}CH\cdot CH_2\cdot CO\cdot NH_2,$$

identical with the asparaginimide described by Körner and Menozzi (Abstr., 1887, 1031); the formula $NH_2\cdot CH{<}{}^{CO-NH}_{CH_2\cdot CO}$, deduced by these authors, should therefore be doubled. E. F. A.

Reduction of α-Oximino-esters; Synthesis of Homologues of Glycine and their Esters. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1904, [iii], **31**, 1176—1180).—The α-oximino-esters may be conveniently reduced to the corresponding α-amino-esters by reduction with either aluminium amalgam or sodium amalgam. In both processes there is formed, in addition to the amino-ester and amino-acid, a small quantity of the ester of the corresponding hydroxy-acid. The reduction of α-oximino-esters to the corresponding amino-esters by aluminium amalgam is somewhat unexpected in view of Bouveault and Wahl's observation that the α-nitroethylenes are converted by this reagent into aldoximes. The further reduction in the present case appears to be due to the influence of the carboxyethyl-group (compare Abstr., 1901, i, 114). When ethyl oximino*iso*butyl-acetate, $CHMe_2\cdot CH_2\cdot C(NOH)\cdot CO_2Et$, is reduced with aluminium amalgam, there is formed some *ethyl α-hydroxyisohexoate*; this is

a colourless, oily liquid, which boils at 82° under 10 mm. pressure and has a sp. gr. 0·9832 at 0°/4°. T. A. H.

New Synthesis of Racemic Leucine. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1904, [iii], **31**, 1180—1183. Compare preceding abstract).—*Ethyl α-aminoisohexoate*, produced by the reduction of ethyl α-oximino*iso*hexoate,

$$CHMe_2 \cdot CH_2 \cdot C(NOH) \cdot CO_2Et,$$

is a colourless, mobile liquid with a disagreeable odour: it boils at 94° under 16 mm. pressure, has a sp. gr. 0·9765 at 0°/4°, and when treated with potassium cyanate furnishes the corresponding *carbamide*, $CHMe_2 \cdot CH_2 \cdot CH(NH \cdot CO \cdot NH_2) \cdot CO_2Et$, which crystallises in white needles from a mixture of ether and light petroleum and melts at 92—93°. On prolonged ebullition with water, the ethyl ester yields the corresponding acid (formed also in the reduction of the oximino-ester), which is identical with *r*-leucine. The synthetic material melted at 290°, the benzoyl derivative at 139—140° (corr.), the benzenesulphonate at 145—146° (corr.), and the 2:5-diketo-3:6-di-*iso*butylpiperazidine (leucinimide), produced by spontaneous change of the ethyl ester, at 265°. These melting points were determined on the Maquenne block and differ slightly from those recorded by Schulze and Likiernik (Abstr., 1891, 681; 1893, i, 309) and Fischer (*ibid.*, 1900, i, 646). T. A. H.

Preparation of Crystallised Taurocholic Acid. OLOF HAMMARSTEN (*Zeit. physiol. Chem.*, 1904, **43**, 127—144).—Crystallised taurocholic acid may be obtained by the following process. A 2 per cent. aqueous solution of the sodium salt is mixed with a 2 per cent. solution of hydrochloric acid, then saturated with sodium chloride, filtered if necessary, and mixed with ether and shaken, when crystals begin to appear after several hours. A simpler method is to dissolve the taurocholate in alcohol containing a little water, acidify with hydrochloric or sulphuric acid, filter, and then add ether to the filtrate until a marked opalescence is observable. The presence of a small amount of water is absolutely necessary, as otherwise the acid is deposited in an amorphous condition. After several solutions in alcohol and precipitations with ether, the acid is obtained free from mineral matter. The acid obtained from different biles has the same properties. It crystallises in long needles or large prisms, has a characteristic sweet taste, is readily soluble in water or alcohol, but is insoluble in ether, benzene, or acetone, and is not deliquescent. When heated at 100°, it gradually decomposes.

Details are given for the extraction of taurocholic acid from the bile of haddocks, oxen, and dogs. Dogs' bile yields, in addition to the ordinary acid, a second crystalline taurocholic acid with a much more bitter taste. On hydrolysis with 8 per cent. sodium hydroxide at 100°, this acid yields a cholic acid melting at 182°. J. J. S.

The Stereochemistry of Chromium. I. PAUL PFEIFFER [and, in part, P. KOCH, G. LANDO, and A. TRIESCHMANN] (*Ber.*, 1904, **37**, 4255—4290. Compare Abstr., 1900, i, 559, 688; 1901, ii, 659; 1902, i, 138, 728; 1903, i, 464, 612).—The diacidodiethylenediaminechromium

salts, $[En_2CrX_2]X$ (where En = ethylenediamine), can exist in two stereoisomeric modifications, the *cis*- and *trans*-forms. The dithiocyanodiethylenediaminechromium salts described in Abstr., 1902, i, 138 are the *trans*-salts.

cis-*Dithiocyanodiethylenediaminechromium thiocyanate*, prepared by adding potassium thiocyanate to a solution of the *cis*-dichloro-chloride (violet salt), crystallises from warm water in orange scales or needles. No *trans*-salt is produced. A mixture of the two isomerides is obtained on warming potassium chromium thiocyanate with ethylenediamine or on warming the luteo-thiocyanate, $[CrEn_3](SCN)_3$, with potassium thiocyanate, and may be separated by crystallisation from water.

cis-*Dithiocyanodiethylenediaminechromium chloride*,

$$[En_2Cr(SCN)_2]Cl,H_2O,$$

prepared by heating the thiocyanate with hydrochloric acid, forms glistening, ruby-red needles, and is less soluble in water than the *trans*-salt. The cis-*bromide* also contains H_2O, and forms ruby-red, prismatic needles; the cis-*mercuri-iodide*, $[En_2Cr(SCN)_2]I,HgI_2$, is a fine, crystalline, orange precipitate. The *nitrate* forms small, reddish-orange needles. The cis-*hydrogen sulphate* forms star-shaped groups of orange needles containing $1\frac{1}{2}H_2O$.

Bromoaquodiethylenediaminechromium bromide, $[En_2Cr(OH_2)Br]Br_2$, prepared by converting green chromium chloride hydrate into the pyridine compound (Abstr., 1902, i, 728), evaporating with ethylenediamine, and adding fuming hydrobromic acid, crystallises in red leaflets.

cis-*Dichlorodiethylenediaminechromium chloride*, $[En_2CrCl_2]Cl,H_2O$, may be prepared from the pyridine compound and hydrochloric acid, or by heating the luteo-chloride at 160°, or by passing a current of chlorine through an aqueous suspension of the dithiocyano-thiocyanate, and crystallises in reddish-violet needles, becoming anhydrous at 100°. Evaporation with concentrated hydrochloric acid and mercuric chloride partially converts it into the green *trans*-dichloro-chloride.

The cis-*dichloro-bromide* is precipitated by hydrobromic acid in small, violet needles containing H_2O and becoming anhydrous at 100°. The *iodide, nitrate, thiocyanate, dithionate*, and *hydrogen sulphate* form violet needles and are anhydrous; the *platinichloride* forms a violet precipitate and contains $12H_2O$.

trans-*Dichlorodiethylenediaminechromium chloride*, prepared by the action of chlorine on the *trans*-dithiocyano-thiocyanate, forms green or blue, strongly dichroic crystals of the composition

$$[En_2CrCl_2]Cl,HCl,2H_2O,$$

passing into the green, normal chloride at 100°. On evaporating with hydrochloric acid, after exposure to daylight, the violet *cis*-salt is obtained.

The trans-*dichloro-bromide* forms small, rhombic tablets, which are green by reflected, red by transmitted, light. The *iodide, thiocyanate*, and *nitrate* form greyish-green crystals, becoming pure green on heating, but recovering their original colour on cooling.

The configuration of the isomerides is determined by their relation to the oxalo-derivative. On warming the *cis*-dichloro-chloride with potassium oxalate, glistening, carmine-red crystals of a complex *salt*,

$[En_2Cr(C_2O_4)][EnCr(C_2O_4)_2],1\frac{1}{2}H_2O$, are obtained, becoming anhydrous at 100°. Hydrobromic acid converts it into Werner and Schwarz's oxalobromide, $[En_2Cr(C_2O_4)]Br$. The *trans*-chloride, on similar treatment, yields a red, complex salt containing the unaltered *trans*-dichloro-group, $[En_2CrCl_2]$. Hydrochloric acid converts the oxalodiethylenediaminechromium iodide into the *cis*-dichloro-iodide, no *trans*-compound being produced.

The stereochemical relations of the compounds described are summarised in tabular form, and a comparison is made between the complex chromium and cobalt salts. C. H. D.

Action of Acid Amides on Aldehydes. ALBERT REICH (*Monatsh.*, 1904, **25**, 933—942).—*iso*Butaldehyde and formamide, when heated together at 170—180° in presence of pyridine, form a small amount of iso*butylidenediformamide*, $CHMe_2{\cdot}CH(NH{\cdot}COH)_2$, which crystallises in colourless needles, melts at 172°, decomposes when distilled under reduced pressure, is easily soluble in ether, less so in alcohol, and only slightly so in water, and is hydrolysed by dilute sulphuric acid, the product reducing ammoniacal silver solution and yielding ammonia when warmed with aqueous potassium hydroxide.

Propaldehyde and acetamide react at 170—180° in presence of pyridine to form *propylidenediacetamide*, $CHEt(NHAc)_2$, which crystallises in small, silky needles, melts at 188°, decomposes when distilled, is easily soluble in alcohol, ether, or phenol, and, when boiled with dilute sulphuric acid, is hydrolysed to propaldehyde, ammonia, and acetic acid. G. Y.

Action of Acetamide on Aldehydes, and of Formamide on Acetophenone. MAX REICH (*Monatsh.*, 1904, **25**, 966—978. Compare preceding abstract).—When heated at 180° in presence of pyridine, *iso*butaldehyde and acetamide form iso*butylidenediacetamide*,

$$CHPr^{\beta}(NHAc)_2,$$

which crystallises in colourless needles, commences to sublime at 214°, melts and decomposes at 216°, is easily soluble in alcohol, ether, phenol, or bromoform, and is hydrolysed by boiling dilute sulphuric acid or 10 per cent. aqueous potassium hydroxide to *iso*butaldehyde, ammonia, and acetic acid.

Hexaldehyde and acetamide, in presence of pyridine at 180—185°, form *hexylidenediacetamide*, $CH_2Pr^{\alpha}{\cdot}CH_2{\cdot}CH(NHAc)_2$; it crystallises in leaflets, melts at 145°, is easily soluble in alcohol, ether, or phenol, and is hydrolysed by dilute sulphuric acid to hexaldehyde, ammonia, and acetic acid.

When heated with zinc chloride at 170—180°, acetophenone and formamide yield *s*-triphenylbenzene and a substance which crystallises in leaflets and small, slender needles, melts at 60°, has a slight, pleasant odour, does not evolve ammonia when treated by Kjeldahl's nitrogen method, and is probably a mixture of phenylpyrimidine (9 parts) and diphenylpyridine (2 parts). G. Y.

5 : 5-Dialkylbarbituric Acids and the Ureides of the Dialkylacetic Acids. EMIL FISCHER and ALFRED DILTHEY (*Annalen*, 1904, **335**, 334—368).—5 : 5-Diethylbarbituric acid (Conrad and Guthzeit,

Abstr., 1883, 314) is formed (yield, 70 per cent. of the theoretical) by the action of sodium ethoxide on ethyl diethylmalonate and carbamide in absolute alcoholic solution at 105—108°, or by the action of diethylmalonic chloride on carbamide. It crystallises from water in large, colourless, spear-like crystals, melts at 191° (corr.), sublimes slowly at 100°, is moderately soluble in hot water or alcohol, but only slightly so in ether, and has a bitter taste; it has a slightly acid reaction to litmus, and is easily soluble in aqueous alkali hydroxides, ammonia, calcium hydroxide, or baryta solutions. The *sodium* salt, $C_8H_{11}O_3N_2Na$, forms glistening crystals and is decomposed by carbon dioxide in aqueous solution.

5 : 5-Dimethylbarbituric acid is formed, in a yield of 39 per cent. of the theoretical, by the condensation of ethyl dimethylmalonate with carbamide in presence of sodium ethoxide. It crystallises from methyl alcohol in leaflets, melts at 279° (compare Thorne, Trans., 1881, **39**, 545), and is more soluble in water than the diethyl acid. The *sodium* salt, $C_6H_6O_3N_2Na_2$, is obtained as a white, crystalline mass.

5-*Methyl*-5-*ethylbarbituric acid*, $CMeEt<\genfrac{}{}{0pt}{}{CO\cdot NH}{CO\cdot NH}>CO$, crystallises in long, flat needles and melts at 212° (corr.). 5-*Methyl*-5-*propylbarbituric acid* melts at 182° (corr.). 5 : 5-*Dipropylbarbituric acid*,

$$CPr_2<\genfrac{}{}{0pt}{}{CO\cdot NH}{CO\cdot NH}>CO,$$

prepared by the condensation of ethyl dipropylmalonate and carbamide in presence of sodium ethoxide, or by the action of dipropylmalonic chloride on carbamide, crystallises in colourless plates and melts at 145° (corr.); the *sodium* salt, $C_{10}H_{15}O_3N_2Na$, crystallises in short prisms. 5-*Ethyl*-5-*propylbarbituric acid* crystallises in long, colourless, glistening needles and melts at 146° (corr.). 5 : 5-*Diisobutylbarbituric acid* crystallises in thin, colourless leaflets and melts at 173·5° (corr.). 5 : 5-*Diisoamylbarbituric acid* crystallises in slender, colourless needles and melts at 172° (corr.). 5 : 5-*Dibenzylbarbituric acid* crystallises in colourless plates and melts at 222° (corr.).

1-*Methyl*-5 : 5-*diethylbarbituric acid*, $CEt_2<\genfrac{}{}{0pt}{}{CO\cdot NMe}{CO-NH}>CO$, obtained from ethyl diethylmalonate and methylcarbamide, forms colourless needles and melts at 154·5° (corr.). 1-*Phenyl*-5 : 5-*diethylbarbituric acid*, $CEt_2<\genfrac{}{}{0pt}{}{CO\cdot NPh}{CO-NH}>CO$, crystallises in thin, colourless, glistening leaflets and melts at 197° (corr.). 1 : 3 : 5 : 5-*Tetraethylbarbituric acid*, $CEt_2<\genfrac{}{}{0pt}{}{CO\cdot NEt}{CO\cdot NEt}>CO$, prepared by the action of diethylmalonic chloride on *s*-diethylcarbamide at 120—130°, is a colourless oil, boils at 125·5—126° (corr.) under 8·8 mm. pressure, has an ester odour, and is volatile with steam.

3-*Thio*-5 : 5-*diethylbarbituric acid*, $CEt_2<\genfrac{}{}{0pt}{}{CO\cdot NH}{CO\cdot NH}>CS$, obtained by the condensation of ethyl diethylmalonate with thiocarbamide in presence of sodium ethoxide at 105°, crystallises in yellow needles, melts at 180° (corr.), and is moderately soluble in hot water, from which it crystallises in flat plates or prisms.

5 : 5-*Diethylmalonylguanidine*, $CEt_2<\genfrac{}{}{0pt}{}{CO\cdot NH}{CO\cdot NH}>C{:}NH$, formed from ethyl diethylmalonate and guanidine in presence of sodium ethoxide, or by the action of diethylmalonic chloride or guanidine, crystallises in slender, colourless needles and decomposes without melting when heated. 5 : 5-*Dipropylmalonylguanidine* crystallises in white leaflets or plates, melts at 93°, and forms a crystalline *nitrate*; the *hydrochloride* crystallises in slender needles or thick prisms.

5-*Methylbarbituric acid*, $CHMe<\genfrac{}{}{0pt}{}{CO\cdot NH}{CO\cdot NH}>CO$, obtained by the condensation of ethyl methylmalonate and carbamide in presence of sodium ethoxide, crystallises in microscopic plates or prisms, melts at 202—203° (corr.), has an acid taste and reaction, and is easily soluble in boiling water, but only slightly so in alcohol; the *sodium* salt, $C_{10}H_{11}O_6N_4Na$, forms small, rose-coloured crystals, and, on addition of the calculated quantity of a mineral acid, yields the *neutral sodium* salt. 5-Ethylbarbituric acid is found to melt at 194° (corr.) (compare Conrad and Guthzeit, *loc. cit.*); when dissolved in aqueous sodium hydroxide and treated with ethyl iodide, it yields diethylbarbituric acid. 5-*Propylbarbituric acid*, $CHPr<\genfrac{}{}{0pt}{}{CO\cdot NH}{CO\cdot NH}>CO$, melts at 208° (corr.); 5-iso*propylbarbituric acid* crystallises in long, thin plates and melts at 216° (corr.).

5-*Bromo*-5-*methylbarbituric acid*, $CBrMe<\genfrac{}{}{0pt}{}{CO\cdot NH}{CO\cdot NH}>CO$, formed by shaking methylbarbituric acid with bromine water, forms colourless crystals, melts at 192·5° (corr.), and, when treated with alcoholic ammonia, yields 5-*methyluramil*, $NH_2\cdot CMe<\genfrac{}{}{0pt}{}{CO\cdot NH}{CO\cdot NH}>CO$, which separates from water in colourless crystals, melts at 237° (corr.), and is more stable towards oxidising agents than is uramil. 5-*Ethyluramil*, $NH_2\cdot CEt<\genfrac{}{}{0pt}{}{CO\cdot NH}{CO\cdot NH}>CO$, obtained from ethylbromobarbituric acid (Conrad and Guthzeit), melts and undergoes slight decomposition at 216° (corr.).

The ureides of dialkylmalonic acids are formed, sometimes along with the ureides of the corresponding dialkylacetic acids, by the action of fuming sulphuric acid on the mixture of dialkylmalonic acid and carbamide. *Ureidodiethylmalonic acid*, $NH_2\cdot CO\cdot NH\cdot CO\cdot CEt_2\cdot CO_2H$, crystallises in thin, colourless leaflets, melts and decomposes at 162° (corr.), and has an acid taste and reaction. *Ureidodipropylmalonic acid*, $NH_2\cdot CO\cdot NH\cdot CO\cdot CPr_2\cdot CO_2H$, melts and decomposes at 147° yielding *dipropylacetylcarbamide*, which crystallises in slender needles and melts at 192·5°.

The action of fuming sulphuric acid on a mixture of dimethylmalonic acid and carbamide leads to the formation of 5 : 5-dimethylbarbituric acid.

The ureides of dialkylacetic acids are also formed by the action of phosphorus oxychloride on a mixture of the acid and carbamide. α-*Ethylbutyrylcarbamide*, $CHEt_2\cdot CO\cdot NH\cdot CO\cdot NH_2$, crystallises in colourless, slender needles, melts at 207·5° (corr.), is moderately soluble in

hot water, and is insoluble in dilute alkali hydroxides. When heated with hydrochloric acid of sp. gr. 1·19 in a sealed tube at 100°, it is hydrolysed with formation of α-ethylbutyric acid and carbamide. *α-Methylbutyrylcarbamide*, $CHMeEt\cdot CO\cdot NH\cdot CO\cdot NH_2$, crystallises in colourless needles, melts at 178·5° (corr.), and is easily soluble in hot water. G. Y.

Influence of the Nature of the Anode on the Electrolytic Oxidation of Potassium Ferrocyanide. André Brochet and Joseph Petit (*Compt. rend.*, 1904, **139**, 855—857. Compare Abstr., 1903, ii, 352; 1904, ii, 229, 230, 414).—When a solution of potassium ferrocyanide is electrolysed in a vessel provided with a diaphragm, potassium ferricyanide and ferrocyanic acid are formed at the anode by the action of the anion, $\overset{iv}{Fe(CN)_6}$, on the potassium ferrocyanide and the water respectively according to the equations:

$$(1)\ 2\overset{iv}{Fe(CN)_6} + 6K_4Fe(CN)_6 = 8K_3Fe(CN)_6;$$

$$(2)\ \overset{iv}{Fe(CN)_6} + 2H_2O = H_4Fe(CN)_6 + O_2.$$

If, however, the anode is a metal capable of forming a ferrocyanide, the yield of the ferricyanide is diminished; and of the sixteen different metals examined in this respect, good yields of ferricyanide were obtained with such metals as platinum, which does not form a ferrocyanide, iron, which does not readily do so, and with copper, which is readily attacked, whilst magnesium, aluminium, and silver behaved like soluble anodes. The experiments were conducted in a nickel vessel which served as cathode, provided with a porous cell containing the anode; at the end of each experiment, the anode solution was measured, the unchanged ferrocyanide in a definite volume estimated by means of potassium permanganate in acid solution (Haen's method); in another quantity of the solution, the ferricyanide was reduced by means of hydrogen peroxide in alkali solution, and the total ferrocyanide estimated; the difference between the two results gave the amount of salt oxidised by electrolysis. M. A. W.

Blue Iron-cyanogen Compounds. Karl A. Hofmann, O. Heine, and F. Höchtlen (*Annalen*, 1904, **337**, 1—36. Compare Abstr., 1900, i, 591).—In a detailed investigation of the properties and composition of the blue compounds obtained from ferrous and ferric salts and ferro- and ferri-cyanides, it is shown that the soluble Prussian blue prepared from potassium ferrocyanide (1 mol.) and a ferric salt (less than 1 mol.) is identical with soluble Turnbull's blue, prepared from potassium ferricyanide (1 mol.) and a ferrous salt (less than 1 mol.). Both are potassium ferric ferrocyanides, their composition corresponding very nearly with the formula $Fe(CN)_6KH_2Fe(OH)_2$ (compare Skraup, *Annalen*, 1877, **186**, 371).

The insoluble Prussian blue, which is obtained by addition of excess of a ferric salt or a mixture of a ferrous and a ferric salt to potassium ferrocyanide, is identical with the insoluble Turnbull's blue prepared by addition of excess of a ferrous salt to potassium ferri-

cyanide and washing the solid with full exposure to air. Both are ferric ferrocyanides, $Fe_4[Fe(CN)_6]_3,10H_2O$.

The insoluble greenish-yellow, crystalline solid remaining after the preparation of prussic acid is not identical with the precipitates obtained from ferrous salts and ferrocyanides. These precipitates are readily oxidised by the air to soluble or insoluble Prussian blue, whilst the residue is incompletely oxidised by the air, but oxidised by hydrogen peroxide to Williamson's violet. Although this violet has a composition identical with that of soluble Prussian blue, it differs from it in many respects, more especially in being more stable towards alkalis. It is suggested that it is a polymeride, and probably has the composition represented by the formula

$$KH[Fe(CN)_6]<^{Fe(OH)}_{Fe(OH)}>[Fe(CN)_6]KH.$$

In that case, the residue from the preparation of prussic acid has the constitution $K_2[Fe(CN)_6]<^{Fe}_{Fe}>[Fe(CN)_6]K_2$, being the corresponding ferrous salt.

The blue compounds, Prussian blue, Turnbull's blue, and Williamson's violet, are all obtained when a mixture of ferricyanide and ferric salt is reduced by a reagent which will reduce the ferricyanide but not the ferric salt; such a reagent is hydrogen peroxide. In neutral or feebly acid solution, Prussian or Turnbull's blue is formed, whilst in strongly acid solution Williamson's violet is produced. These facts all demonstrate that in these substances ferric iron is combined with ferrocyanide and in no case ferricyanide with ferrous iron.

Attempts to prepare ferric ferrocyanide by the action of alcoholic ferric chloride on ferrocyanic acid led to the production of substances which contain both chlorine and alcohol. According to the proportions used and the conditions, temperature, &c., two or three different compounds were formed; they are dark blue powders and appear to be ferric ferrocyanides in which chlorine is still combined with the iron, and in which ethyl groups partly replace the hydrogen of the ferrocyanic acid. K. J. P. O.

Electrolytic Preparation of Barium Platinocyanide. André Brochet and Joseph Petit (*Bull. Soc. chim.*, 1904, [iii], **31**, 1265—1269. Compare Abstr., 1904, ii, 414).—A solution of barium cyanide, prepared by adding hydrocyanic acid to barium hydroxide suspended in water, is electrolysed in a vessel closed by a caoutchouc stopper provided with four holes, two of which carry the wires leading to the electrodes, the third a thermometer, and the fourth a funnel closed by glass wool to absorb splashes of liquid. The electrodes consist of sheet platinum suspended by thick platinum wire. The current employed is about 20 amperes, and the whole apparatus is placed in a bath of water so that the temperature of the electrolyte is between 50° and 60° and the operation is continued for about 8 hours. Carbon dioxide is then passed through the liquid and the precipitate filtered off, washed, and the filtrate and washings concentrated. On cooling, some barium platino cyanide crystallises out, and more may be procured by evaporating the mother liquor to dryness and extracting with methyl alcohol. The

platinocyanide may be obtained in small, green crystals by crystallisation from solutions of barium cyanide, and in this condition is markedly fluorescent. This form has the same composition as the ordinary platinocyanide, $BaPt(CN)_4,4H_2O$, and not, as stated by Dammer, that represented by the formula $Ba_6Pt_5(CN)_{22},22H_2O$. T. A. H.

Theory of the Grignard Reaction and a New Method for the Preparation of Organo-magnesium Compounds. WLADIMIR TSCHELINZEFF (*Ber.*, 1904, **37**, 4534—4540).—Grignard's organo-magnesium compounds may be prepared in the presence of benzene to which a small amount of ether or anisole has been added, or even in benzene or toluene solution alone if a sufficiently high temperature is employed (compare Brühl, Abstr., 1903, i, 314; 1904, i, 139, 435; Malmgren, Abstr., 1903, i, 710). The ether thus appears to be a catalytic agent, and the reaction is represented as occurring in the two stages: $R_2O + R'X = R_2O{<}^{R'}_{X}$ and $R_2O{<}^{R'}_{X} + Mg = R{\cdot}Mg{\cdot}X + R_2O$.

When only a small amount of ether, or when no ether, is used, the organo-magnesium compound separates as a solid without ether of crystallisation. It is also shown that a small amount of a tertiary amine, dimethylaniline, can be used in place of ether for the preparation of organo-magnesium compounds in the presence of benzene, hexane, turpentine, &c. The magnesium compound separates as a white, flocculent mass having the composition $R{\cdot}Mg{\cdot}X$. J. J. S.

Electrolytic Oxidation of the Hydrocarbons of the Benzene Series. I. Hydrocarbons containing the Methyl Group. H. D. LAW and F. MOLLWO PERKIN (*Trans. Faraday Soc.*, 1904, **1**, Reprint, 1—11).—When an emulsion of toluene with dilute acid or alkali is electrolysed, complete oxidation to carbon dioxide and water takes place. The electrolytic oxidation is best carried out by dissolving the hydrocarbon in acetone and stirring with 20 per cent. sulphuric acid in the anode cell, anodes of platinum gauze being employed. Lead cathodes in a solution of sulphuric acid or sodium sulphate are used. The current density is 1—2 amperes at the anode and the *E.M.F.* about 4 volts; the temperature must be kept low.

In each of the cases examined, the product is the aldehyde, a small quantity of a neutral compound, probably the corresponding alcohol, being formed at the same time. When several methyl groups are present, only one of them is oxidised to the aldehydic group. The addition of oxygen carriers has no influence on the result.

o-*Tolualdehydesemicarbazone* crystallises from amyl alcohol in small, white needles melting at 196°; p-*tolualdehydesemicarbazone* forms small, white plates melting at 215°; the *phenylhydrazone* is yellow, becoming red on exposure to light, and melts at 113°. The mixture of monoaldehydes obtained from ψ-cumene yields a *semicarbazone*, forming pearly-white plates and melting at 215·5°. 3 : 5-*Dimethylbenzaldehyde*, obtained from mesitylene, boils at 218—219°; the *semicarbazone* forms pearly plates and melts at 201·5°. C. H. D.

Fluorobenzene and some of its Derivatives. [Arnold F. Holleman and] J. W. Beekman (*Rec. Trav. Chim.*, 1904, **23**, 225—256). —Most of the results given in this paper have already appeared in Abstr., 1904, i, 232 and 486. The present paper gives in addition details of the methods and apparatus employed and the yields of the various products obtained. T. A. H.

Simultaneous Formation of Isomeric Substitution Derivatives of Benzene. X. Nitration of Dichlorobenzenes. Arnold F. Holleman (*Rec. Trav. Chim.*, 1904, **23**, 357—379. Compare Abstr., 1899, i, 759; 1900, i, 387, 638; 1901, i, 318, 591; 1902, i, 87; and 1903, i, 623).—The dichlorobenzenes were added drop by drop to nitric acid cooled to 0° or −30°. In the case of *o*-dichlorobenzene, the principal product in each case was 1 : 2-dichloro-4-nitrobenzene, and there was formed of the accessory product, 1 : 2-dichloro-3-nitrobenzene, 7·2 per cent. at 0° and 5·2 per cent. at −30°. With *m*-dichlorobenzene, the principal product was 1 : 3-dichloro-4-nitrobenzene, and the accessory product, 1 : 3-dichloro-2-nitrobenzene, was formed to the extent of 3·8 to 4·3 per cent. and 2·5 to 2·7 per cent. at 0° and −30° respectively. From the data available, it was considered unlikely that any 1 : 3-dichloro-5-nitrobenzene was formed in this reaction. The proportions of the respective isomerides formed were calculated by the methods already described (*loc. cit.*). The results obtained, taken in conjunction with those previously recorded (*loc. cit.*), show that the amount of accessory product formed increases with rise of temperature. In the nitration of dichlorobenzenes, the nitro-group takes up either the ortho- or para-position with regard to one chlorine atom, and the two positions which may be occupied are symmetrical with regard to the second atom of chlorine. The amount of accessory product formed during nitration is less in the case of the dichlorobenzenes and the halogenated benzoic acids (Abstr., 1900, i, 387 and 591) than in the case of chlorobenzene; this is due to the influence of the second chlorine atom and of the carboxyl group in the two cases, and the effect is about twice as great when the perturbing group is in the *o*-position as when it occupies the *m*-position. 1 : 2-Dichloro-3-nitrobenzene, produced together with 1 : 4-chloro-3-nitrobenzene and hexachlorobenzene (?) by chlorinating *o*-chloronitrobenzene in presence of antimony chloride, is separated from its isomeride by fractional distillation and recrystallisation from acetic acid; it crystallises in silky needles and melts at 59·9°, boils at 257—258°, and has a sp. gr. 1·4494 at 79·5° (compare Beilstein and Kurbatoff, Abstr., 1876, 632). 1 : 2-Dichloro-4-nitrobenzene melts at 43°, solidifies at 40·5°, boils at 255—256°, and has a sp. gr. 1·4514 at 80·18° (compare Beilstein and Kurbatoff, Abstr., 1875, 450). 1 : 3-Dichloro-2-nitrobenzene, obtained from *p*-nitroaniline by the method described by Beilstein and Kurbatoff (Abstr., 1879, 143), which was simplified in various ways, crystallises from alcohol and melts at 70°, solidifies at 70·05°, boils at 130° under 8 mm. pressure, and has a sp. gr. 1·4094 at 79·9°. 1 : 3-Dichloro-4-nitrobenzene (Beilstein and Kurbatoff, Abstr., 1876, 632) melts at 31·5° to 32°, solidifies at 30·45°, boils at 258·5°, and has a sp. gr. 1·4390 at 79·7°. 1 : 3-Dichloro-5-nitrobenzene (Abstr., 1875, 450),

prepared by chlorinating *p*-nitroaniline and diazotising the 2 : 6-dichloro-3-nitroaniline so produced, melts at 65°, solidifies at 63·15°, and has sp. gr. 1·4278 at 80·6°.

The specific gravities of the series of dinitroanisoles and dichloronitrobenzenes are tabulated in the original; the table shows that there is a fairly constant difference between the specific gravities of the ortho- and meta-isomerides in the two series. T. A. H.

Nitration of Disubstituted Benzenes. ARNOLD F. HOLLEMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, **7**, 266—269. Compare Abstr., 1903, i, 623).—In the nitration of chlorobenzene at 0°, 29·8, 0·3, and 69·9 per cent. of *o*-, *m*-, and *p*-chloronitrobenzenes are respectively formed, whilst in the nitration of benzoic acid, 18·5, 80·2, and 1·3 per cent. of *o*-, *m*-, and *p*-nitrobenzoic acids are respectively formed. If the carboxyl and chlorine groups did not modify each other's directing influence, the nitro-derivatives obtained in the nitration of *o*-chlorobenzoic acid would be formed in the proportion represented by $(29·8 \times 80·2):(69·9 \times 80·2)$, whilst in the nitration of *m*-chlorobenzoic acid the proportion would be represented by $(29·8 \times 18·5):(69·9 \times 18·5)$; the proportions actually found in such cases were, however, 16 : 84 and 8·7 : 91·3 respectively.

Other similar cases are also quoted. A. McK.

Action of Potassium Cyanide on ω-Nitrostyrolene [β-Nitrostyrene]. M. HOLLEMAN (*Rec. Trav. Chim.*, 1904, **23**, 283—297).—When β-nitrostyrene, dissolved in alcohol, is treated with an aqueous solution of potassium cyanide and the mixture is acidified with acetic acid, there is precipitated the *α-form* of *αδ-dinitro-β-cyano-αβ-diphenylbutane*, $NO_2·CH_2·CPh(CN)·CHPh·CH_2·NO_2$, whilst the *β-isomeride* of this remains dissolved and can be obtained by addition of excess of water. The α-form is colourless, crystallises from acetone on addition of light petroleum, and melts at 180° to 215° according to the rate of heating. The β-form crystallises from warm alcohol and melts and decomposes at 110·5°. Both forms, when heated with mineral acids in closed tubes, furnish diphenylsuccinic acid, hydroxylamine, and carbon dioxide and, when treated with alkalis, α-nitroacetophenone and hydrogen cyanide. Both isomerides reduce ammoniacal silver nitrate solution in the cold and the α-form is oxidised by potassium permanganate forming nitrous and benzoic acids. The formation of αδ-dinitro-β-cyano-αβ-diphenylbutane from β-nitrostyrene is explained in a manner analogous to that suggested by Poppe for the production of diethyl cyanodiphenylsuccinate by the action of potassium cyanide on ethyl α-bromophenylacetate (Abstr., 1890, 504). T. A. H.

Formation of 2-Acetyl-1 : 3-diketohydrindene by the Interaction of Phthalyl Chloride and Acetylacetone. CARL BÜLOW and MAX DESENISS (*Ber.*, 1904, **37**, 4379—4382).—Sodioacetylacetone reacts in ethereal solution with phthalyl chloride forming *phthalylacetylacetone*, $CO<\genfrac{}{}{0pt}{}{C_6H_4}{-O-}>C:C(CMe)_2$, which crystallises in colourless needles or rhombic plates melting at 129°. At the same time, owing to the

further action of the acid chloride on the acetylacetone, phthalylacetonylene is formed, which at once undergoes rearrangement into 2-acetyl-1 : 3-diketohydrindene melting at 110°. The presence of small quantities of phthalic acid, acetic acid, and acetylacetone in the ethereal solution was confirmed. E. F. A.

Action of Methylene Chloride and Aluminium Chloride on Toluene. JAMES LAVAUX (*Compt. rend.*, 1904, **139**, 976—978).—The author finds that the compound melting at 232° obtained by Friedel and Craft by the action of methylene chloride and aluminium chloride on toluene (Abstr., 1887, 1102), and described as dimethylanthracene, is a mixture of three isomeric dimethylanthracenes melting at 240°, 244·5°, and 86° respectively, and of β-monomethylanthracene. Anschütz's dimethylanthracene, melting at 225° and obtained by the action of *s*-tetrabromoethane and aluminium chloride on toluene (Abstr., 1885, 768), is a similar mixture, but contains none of the isomeride melting at 86°. In addition to the anthracene derivatives already described, di-*m*- and di-*p*-tolylmethanes are also produced, together with benzene, xylene, and their homologues, by the action of methylene chloride and aluminium on the toluene, and the course of the reaction appears to be (1) the formation of the ditolylmethane derivatives by the direct action of toluene on the methylene chloride, (2) the interaction of this compound with a second molecule of methylene chloride to form a hydride of dimethylanthracene, which reacts with a third molecule of the chloride to form methyl chloride and the corresponding anthracene derivative, (3) the xylene is formed by the interaction of the methyl chloride and toluene in the presence of aluminium chloride, (4) the benzene is formed from the toluene by the action of aluminium chloride, and, finally, (5) the β-monomethylanthracene is the product of the reaction of benzene and toluene with methylene chloride. M. A. W.

Studies in the Phenanthrene Series. XVI. 9 : 10-Dichloro- and 9 : 10-Dibromo-phenanthrenes. A New Mode of Formation of *o*-Dichlorobenzene. JULIUS SCHMIDT and GUSTAV LADNER (*Ber.*, 1904, **37**, 4402—4405. Compare Abstr., 1904, i, 1035).—9 : 10-*Dichlorophenanthrene*, prepared by heating 9-bromo-10-nitrophenanthrene with ammonium chloride for 6 hours at 320°, separates from alcohol in needles and melts at 160—161°. It may also be prepared by the action of chlorine on phenanthrene.

Similarly, *o*-chlorobenzene may be prepared by heating *o*-bromonitrobenzene with ammonium chloride for 12 hours at 320°. This method may possibly be a general one for the preparation of *o*-dichloro-substitution products of aromatic compounds.

9 : 10-*Dibromophenanthrene*, prepared in a similar manner from 9-bromo-10-nitrophenanthrene and ammonium bromide, separates from alcohol in needles and melts at 181—182°. A. McK.

Certain Tri-*p*-tolylmethane Derivatives. N. E. TOUSLEY and MOSES GOMBERG (*J. Amer. Chem. Soc.*, 1904, **26**, 1516—1523).—It has been shown by Gomberg and Voedisch (Abstr., 1901, i, 374) that by

the action of aluminium chloride on a mixture of carbon tetrachloride and toluene a tritolylchloromethane is produced. A further investigation of this substance has proved it to be the tri-*p*-tolyl derivative.

Tri-*p*-tolylchloromethane crystallises from ethyl acetate or light petroleum, melts at 173°, and is readily soluble in benzene, ether, or carbon disulphide. A synthesis of the compound has been effected by the action of magnesium *p*-tolyl iodide on ethyl *p*-toluate.

Tri-p-*tolylcarbinol*, $C(C_6H_4Me)_3{\cdot}OH$, prepared by heating the chloride with a mixture of sulphuric and acetic acids, forms large, colourless crystals, melts at 94°, and is soluble in ether, alcohol, benzene, or carbon disulphide, but only slightly so in light petroleum. An attempt was made to prepare hydroxyphenyltri-*p*-tolylmethane by the condensation of the carbinol with phenol (compare Baeyer and Villiger, Abstr., 1902, i, 769), but without success. The *ethyl* ether, obtained by the action of sodium ethoxide on tri-*p*-tolylchloromethane, crystallises in white, slender needles and melts at 111°. When tri-*p*-tolylcarbinol or its ethyl ether is treated with acetyl chloride, tri-*p*-tolylchloromethane is produced.

Tri-p-*tolylbromomethane*, $C(C_6H_4Me)_3Br$, obtained by the action of hydrogen bromide on tri-*p*-tolylcarbinol, forms yellow crystals and melts at 165°. When this compound is treated with bromine, a *perbromide*, probably a pentabromide, is produced, which forms orange-red crystals. A *periodide* was also obtained which crystallises in dark blue crystals with a metallic lustre and melts at 118—120°; this compound consists either of the tetra- or penta-iodide according to the conditions of the experiment.

When tri-*p*-tolylcarbinol is treated with hydrogen iodide, a *periodide* of tri-*p*-tolyliodomethane is formed, which melts at 138°. By the action of hydrogen iodide on a solution of tri-*p*-tolylcarbinol and iodine in carbon disulphide, the *pentaiodide* of tri-*p*-tolyliodomethane is produced, which forms dark, iridescent crystals and melts at 77°.

Tri-p-*tolylmethane*, $CH(C_6H_4Me)_3$, obtained by the reduction of tri-*p*-tolylchloromethane with zinc and acetic acid, distils at 260—262° under 28 mm. pressure.

When tri-*p*-tolylcarbinol is oxidised with chromic acid, the *acid*, $C(C_6H_4{\cdot}CO_2H)_3{\cdot}OH$, is produced, which, on heating, slowly volatilises without melting; its *lead*, *silver*, and *sodium* salts were prepared.

Tri-p-*tolylaminomethane*, $C(C_6H_4Me)_3{\cdot}NH_2$, obtained by the action of ammonia on tri-*p*-tolylchloromethane, forms white crystals and melts at 112°.

Tri-p-*tolylmethylaniline*, $C(C_6H_4Me)_3{\cdot}NHPh$, formed by the action of aniline on tri-*p*-tolylchloromethane, separates from acetone in white crystals, melts at 64°, and is soluble in ether, light petroleum, or toluene; when boiled with hydrochloric acid, it is converted into tri-*p*-tolylcarbinol, and, if heated with alcohol, tri-*p*-tolylcarbinol ethyl ether is produced. *Tri*-p-*tolylmethyl*-p-*toluidine*,

$$C(C_6H_4Me)_3{\cdot}NH{\cdot}C_6H_4Me,$$

forms white crystals and melts at 151°.

The electrical conductivities of tri-*p*-tolylchloromethane and the corresponding bromo-derivative were determined at 20° in solution in benzonitrile. The results show that both compounds exhibit con-

siderable conductivity, that of the bromide being almost three times that of the chloride. When sulphur dioxide is used as the solvent, the molecular conductivity is much higher than when benzonitrile is employed. E. G.

Electrolysis of Acid Solutions of Aniline. LACHLAN GILCHRIST (*J. Physical Chem.*, 1904, **8**, 539—547).—Experiments were made to determine whether chloroaniline could be prepared by the electrolysis of hydrochloric acid solutions of aniline. No chloroaniline was obtained, however, aniline-black being apparently formed in each case. It was found that the decomposition voltage of aniline in either hydrochloric or sulphuric acid is about 0·95 volts, that is, lower than that of either of the acids; this is probably an oxidation potential and explains the non-formation of the chloro-derivative. As the value, however, is higher than the decomposition voltage of hydrobromic acid, it appeared probable that bromoaniline might be obtained electrolytically, and experiments showed that this was the case, crystals of bromoaniline, which melted at 116°, being obtained at the anode, whilst aniline-black was not produced. It was found that the oxidation potential of *m*-nitroaniline was 1·43 volts. L. M. J.

Formation of Protocatechuic Anilide. HUGO SCHIFF (*Bull. Soc. chim.*, 1904, [iii], **31**, 1220—1222).—It is asserted that Thibault's statement (Abstr., 1904, i, 805) that Schiff's process of preparing this anilide yields an impure product is due to an inaccurate reading of the paper describing this method (Abstr., 1883, 335). T. A. H.

Reactions of Ethyl Chlorosulphonate. O. W. WILLCOX (*Amer. Chem. J.*, 1904, **32**, 446—476).—It has been shown by Bushong (Abstr., 1903, i, 732) that ethyl chlorosulphonate reacts with sodium alkyloxides and with aniline as an alkylating agent. The alkylating action of this compound is regarded as being due to its dissociation according to the scheme $Cl{\cdot}SO_2{\cdot}O{\cdot}CH_2Me \rightleftarrows CHMe + Cl{\cdot}SO_2{\cdot}OH$ (Nef, Abstr., 1901, i, 626). The results of the present investigation indicate that a further change takes place involving the dissociation of a part of the chlorosulphonic acid into sulphur trioxide and hydrogen chloride.

When chlorosulphonic acid is added to a well cooled solution of dimethylaniline in chloroform, dimethylaniline hydrochloride and *dimethylanilinesulphurtrioxide*, $NPhMe_2{:}SO_3$, are produced, the latter substance being obtained as a granular precipitate which, when heated to 60°, undergoes a transformation into dimethylaniline-*p*-sulphonic acid.

By the action of ethyl chlorosulphonate on dimethylaniline, ethyl chloride, phenyldimethylethylammonium chloride, and dimethylanilinesulphurtrioxide are obtained. *Phenyldimethylethylammonium platinichloride* crystallises in yellow needles.

Dimethylanilinesulphurtrioxide can also be prepared by the direct union of sulphur trioxide with dimethylaniline. It is decomposed readily by water with formation of dimethylaniline sulphate, $NPhMe_2,H_2SO_4$, which melts at 84—85°, and when heated at 200° is

converted into dimethylaniline-*p*-sulphonic acid. Dimethylanilinesulphurtrioxide combines with acetone with formation of an additive *compound*, $NHPhMe_2 \cdot SO_3 \cdot O \cdot CMe{:}CH_2$ or $NPhMe_2 < \substack{-O- \\ SO_3} > CMe_2$, which forms large prismatic crystals, melts at 76—78°, is soluble in water, and is decomposed by acids or alkalis with production of acetone, sulphuric acid, and dimethylaniline. An additive *compound*, obtained when dimethylanilinesulphurtrioxide is warmed with ethyl malonate, crystallises in white leaflets and is decomposed by aqueous alkali hydroxide with formation of ethyl malonate, sulphuric acid, and dimethylaniline. Dimethylanilinesulphurtrioxide reacts with phenol with formation of *phenyldimethylammonium phenyl sulphate*, $NHMe_2Ph \cdot SO_3 \cdot OPh$, which is a crystalline substance, very soluble in water, and decomposed by aqueous potassium hydroxide into dimethylaniline and potassium phenyl sulphate. When aniline is brought into contact with dimethylanilinesulphurtrioxide, combination takes place, and a wax-like *substance*, $NHMe_2Ph \cdot SO_3 \cdot NHPh$, is produced, which is decomposed by barium hydroxide into dimethylaniline and barium phenylsulphamate. Trimethylethylene unites with dimethylanilinesulphurtrioxide with formation of an indistinctly crystalline *substance*, $NMe_2Ph < \substack{CMe_2 \\ O \cdot SO_2} > CHMe$, which is decomposed by water into dimethylaniline, sulphuric acid, and trimethylethylene.

When a well cooled ethereal solution of diethylamine is treated with ethyl chlorosulphonate, triethylamine hydrochloride and tetraethylammonium chloride are produced together with *diethylsulphamic acid*, $NEt_2 \cdot SO_3H$, which crystallises from benzene in colourless, orthorhombic prisms, melts at 89°, and is soluble in water, forming a solution with a strongly acid reaction. The *ethyl* ester, obtained by the action of sodium ethoxide on diethylsulphamic chloride (Behrend, Abstr., 1884, 285), is a colourless oil of a pleasant odour, which boils at 119° under 15 mm. and at 126° under 22 mm. pressure, but undergoes decomposition when heated under the ordinary atmospheric pressure; this compound does not react at the ordinary temperature with ammonia or diethylamine, and therefore cannot be formed as an intermediate product in the interaction of diethylamine and ethyl chlorosulphonate. Ethyl chlorosulphonate reacts with ammonia with formation of the hydrochlorides of diethylamine and triethylamine, tetraethylammonium chloride, and probably ammonium chloride and ammonium iminosulphonate, $NH(SO_3 \cdot NH_4)_2$, together with small quantities of ethyl ethylsulphamate and ethyl diethylsulphamate. When ethyl chlorosulphonate is added to aniline at the ordinary temperature, ethyl chloride and sulphanilic acid are produced (Wenghöffer, this Journal, 1877, ii, 147); if, however, the reaction is carried out at a low temperature, these substances are not produced, but ethylaniline is obtained together with sulphuric and phenylsulphamic acids, the two latter substances probably being produced by the hydrolysis of phenyliminodisulphonic acid, $NPh(SO_3H)_2$, formed as an intermediate product.

When ethyl chlorosulphonate is heated at 160°, it undergoes decomposition with formation of sulphur dioxide, sulphuric acid, ethylene,

hydrogen chloride, and a charred residue. If the compound is heated at 130° with powdered tin and a trace of iodine, ethylene, sulphur dioxide, stannic chloride, and small quantities of hydrogen chloride are produced.

In the following reactions, ethyl chlorosulphonate behaves not as an alkylating, but as a chlorinating agent. It reacts with ethyl sodioacetoacetate with formation of ethyl α-chloroacetoacetate and small quantities of ethyl diacetylsuccinate. When ethyl sodiomalonate is similarly treated, ethyl acetylenetetracarboxylate is produced together with sodium ethyl sulphite and ethyl alcohol.

Ethyl hypochlorite also behaves as a chlorinating agent in its reaction with ethyl sodioacetoacetate and other compounds, such as sodium phenoxide, diethylamine, and trimethylethylene.

When ethyl chlorosulphonate is added to sodium phenoxide suspended in ether at 0°, sodium chloride, sodium sulphate, and phenetole are produced. E. G.

Ethylsulphone Derivatives of *p*-Phenetidine and their Pharmacological Importance. WILHELM AUTENRIETH and R. BERNHEIM (*Arch. Pharm.*, 1904, **242**, 579—589).—*Ethylsulphone-*p*-phenetidine*, $OEt \cdot C_6H_4 \cdot NH \cdot SO_2Et$, was prepared from *p*-phenetidine (2 mols.) and ethylsulphonic chloride (1 mol.) in benzene solution; it melts at 80—81° and has the character of a monobasic acid. Its *acetyl* derivative melting at 78° and *benzoyl* derivative (obtained by heating it with benzoyl chloride at 130°, not by the Schotten-Baumann method) melting at 117° have no acid character. The *methyl* and *ethyl* derivatives melt at 49° and 57° respectively, and have no acid character. A *carbethoxy*-derivative was obtained by the action of alcoholic sodium ethoxide and ethyl chloroformate in succession; it melts at 112° and is poisonous. By nitration with dilute nitric acid (1 : 2) at the atmospheric temperature, or with gentle heat, o-*nitro*-n-*ethylsulphone*-p-*phenetide* [$OEt : NO_2 : N$, &c., $= 1 : 3 : 4$] was obtained; it melts at 179° and is soluble in alkalis.

Ethyl p-*phenetidine*-N-*carboxylate*, $OEt \cdot C_6H_4 \cdot NH \cdot CO_2Et$, was obtained from *p*-phenetidine (2 mols.) and ethyl chlorocarbonate (1 mol.) in benzene solution; it melts at 93·5°; the hydrogen of its imino-group is not replaceable by metals or alkyl or acyl groups.

As was expected, to the antipyretic and antineuralgic properties conditioned by the *p*-phenetidine nucleus, *n*-ethylsulphone-*p*-phenetidine joins a certain sedative and hypnotic action due to the ethylsulphone group. Contrary to expectation, its carbethoxy-derivative, which contains yet another ethyl group, has no hypnotic action at all, instead of an increased one. C. F. B.

Iron Compounds of Salicylic Acid. LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1904, **242**, 563—566).—When the violet liquid obtained by mixing aqueous solutions of ferric chloride and salicylic acid is shaken repeatedly with fresh quantities of ether or chloroform, the colour changes to red and finally disappears, whilst salicylic acid passes into the extract and colloidal ferric hydroxide remains in the aqueous solution. The violet colour is always obtained in the presence of a

certain amount of acid, the red colour when the acidity is small. It is suggested that these two colours correspond with two iron derivatives of salicylic acid, one of which may be derived from a ketonic form of the acid. C. F. B.

Reversion of some Secondary Cyclic Amines. PAUL LEMOULT (*Compt. rend.*, 1904, **139**, 978—980).—Secondary amines of the type NHPhR, where R represents an alkyl group, undergo a reversion into aniline, the alkyl chloride RCl being evolved (compare Hess, Abstr., 1885, 783; Auger, Abstr., 1904, i, 805), when they are allowed to interact with phosphorus trichloride or pentachloride, and in the case of methylaniline the other products of the reaction are the same as those obtained in similar experiments with the phosphorus chlorides and aniline (compare Abstr., 1903, i, 672; Abstr., 1904, i, 380, 572); thus methylaniline yields, with phosphorus pentachloride, methylchloride, the hydrochloride of trianilinophenylphosphimide, and the anilide of phosphoric acid, and with phosphorus trichloride the same products together with hydrogen phosphide (compare Abstr., 1904, ii, 728) and diphenylamine. M. A. W.

Action of Sulphites on Aromatic Amino- and Hydroxy-compounds. II. HANS TH. BUCHERER (*J. pr. Chem.*, 1904, [ii], **70**, 345—364. Compare Abstr., 1904, i, 309).—The principal part of this paper consists of a discussion of the technical value of the reactions previously described (*loc. cit.*).

The formation of phenolic sulphites from mono- and di-alkylated aromatic amines takes place, in the same manner as from primary aromatic amines, on treatment with sodium hydrogen sulphite. The reverse reaction, the formation of secondary or tertiary amines by the action of a primary or secondary fatty amine and its sulphite on the phenol, or of the fatty amine on the phenolic sulphite, does not take place so easily as do the corresponding reactions with ammonia; thus, the reaction of α-naphthol-4-sulphonic acid with methylamine and methylamine sulphite, or of the sulphite of α-naphthol-4-sulphonic acid and methylamine, takes place at 125—150°, whilst these reactions with ammonia take place energetically at 90°.

The author proposes to use the series of reactions, $R{\cdot}NHR' \rightarrow R{\cdot}O{\cdot}SO_2Na(+NH_2R') \rightarrow R{\cdot}NH_2 \rightarrow R{\cdot}NHR'$, where $R{\cdot}NH_2$ is α-naphthylamine-4-sulphonic acid and R' is an alkyl group, for the preparation of primary, and similarly through $R{\cdot}NR'R''$ for that of secondary fatty amines. G. Y.

Action of Bromodinitrobenzene on Glycine. ANDREA SANNA (*Gazzetta*, 1904, **34**, ii, 221—224).—The action of 1-bromo-2 : 4-dinitrobenzene (1 mol.) on glycine (1 mol.) in pyridine solution yields pyridine hydrobromide and 2 : 4-*dinitroanilinoacetic acid*,

$$C_8H_7O_6N\ [NH{\cdot}CH_2{\cdot}CO_2H : NO_2 : NO_2 = 1 : 2 : 4],$$

which crystallises from alcohol or water in shining, golden-yellow scales melting at 112°; the acid is soluble in acetic acid and, to a slight extent, in benzene, light petroleum, or toluene. All its salts explode when heated rapidly. The *silver* salt, $C_8H_6O_6N_3Ag$, crystallises from

water or alcohol in rose-coloured needles which melt at 240° and are decomposed by boiling water; the *lead* salt crystallises from aqueous alcohol in minute, red needles melting at 173—174°; the *barium* salt is yellow, very soluble in alcohol or water, and melts at 297°; the calcium, mercuric, ferric, magnesium, cadmium, and zinc salts are obtained as red or yellow precipitates. T. H. P.

Iodophenylcarbamides. RICHARD DOHT (*Monatsh.*, 1904, **25**, 943—965).—p-*Iodophenylcarbamide*, $NH_2 \cdot CO \cdot NH \cdot C_6H_4I$, is formed by the action of potassium cyanate on *p*-iodoaniline in glacial acetic acid solution or by the action of hydrochloric acid, potassium iodide, and potassium iodate on phenylcarbamide in boiling aqueous solution. It crystallises in monoclinic leaflets, melts irregularly, the same preparation being found to melt at 288°, 295°, and 300°, and, when boiled with acetic anhydride, yields *p*-iodoacetanilide and acetamide.

o-*Iodophenylcarbamide*, formed by the action of potassium cyanate on *o*-iodoaniline in glacial acetic acid solution, crystallises in needles, melts at 197—198°, is easily soluble in water, benzene, or acetone, and, when boiled with acetic anhydride, yields *o*-iodoacetanilide.

m-*Iodophenylcarbamide*, obtained from *m*-iodoaniline and potassium cyanate, crystallises in doubly refractive plates, melts at 174°, and, with acetic anhydride, yields *m*-iodoacetanilide.

The iodophenylcarbamides form acetyl derivatives when treated with acetyl chloride in pyridine solution. *Acetyl*-p-*iodophenylcarbamide*, $NHAc \cdot CO \cdot NH \cdot C_6H_4I$, crystallises in doubly refractive plates, melts at 248°, and decomposes when heated above its melting point, and is hydrolysed by dilute sulphuric acid to *p*-iodoaniline, acetic acid, carbon dioxide, and ammonia. *Acetyl*-o-*iodophenylcarbamide* crystallises in monoclinic prisms and melts at 182°. *Acetyl*-m-*iodophenylcarbamide* crystallises in monoclinic plates or rhombic prisms and melts at 201°.

When heated with aniline, the iodophenylcarbamides yield *s*-diphenyl carbamide, ammonia, and the corresponding iodoaniline. G. Y.

Persubstituted Dithiobiurets. OTTO C. BILLETER and HENRI RIVIER [and, in part, AL. MARET] (*Ber.*, 1904, **37**, 4317—4326. Compare Abstr., 1893, i, 575; Freund, Abstr., 1895, i, 576; Johnson, Abstr., 1903, i, 751).—Persubstituted normal dithiobiurets, containing an aryl group attached to the central nitrogen atom ("mesoaromatic"), undergo rearrangement with hydrogen chloride in chloroform solution, yielding the hydrochlorides of the isomeric ψ-dithiobiurets. In the case of unsymmetrical compounds, a mixture of the two isomeric ψ-compounds is obtained if the substituted amino-groups differ but little from one another (as NPhMe and NPhEt), but when the difference is considerable (as NMe_2 and NPhEt), only one compound is obtained. When an alkyl group is attached to the central nitrogen atom ("mesoaliphatic"), hydrogen chloride does not cause rearrangement, but the molecule is completely broken down.

Of the isomeric ψ-dithiobiurets, that compound is designated by α in which the amine residue of lower molecular weight is attached to the thiocarbonyl, the other isomeride being β.

Symmetrical.—ac-*Diphenyldimethyl*-1-*phenyl*-ψ-*dithiobiuret*, NPhMe·CS·S·C(NPh)·NPhMe, forms pale yellow tablets melting at 139°, but is converted on slowly heating into the normal compound, NPhMe·CS·NPh·CS·NPhMe, which forms yellow needles melting at 203°. ac-*Diphenyldiethyl*-1-*phenyl*-ψ-*dithiobiuret* melts at 120° and the normal *compound* at 158·5°. ac-*Diphenyldipropyl*-1-*phenyl*-ψ-*dithiobiuret* forms a crystalline powder melting at 85·5—86°; it slowly passes in alcoholic solution into the sparingly soluble normal *compound* melting at 158—158·5°.

ac-*Diphenyldiethyl*-1-α-*naphthyl*-ψ-*dithiobiuret* forms pale yellow prisms melting at 113·5—114°, and is converted on boiling its alcoholic solution into the normal *compound* melting at 158—158·5°. The β-*naphthyl*-ψ-compound melts at 127·5—128°, and the normal *compound* at 130—130·5°.

Unsymmetrical.—α-*Diphenylmethylethyl*-1-*phenyl*-ψ-*dithiobiuret* forms yellow needles melting at 118—119°; the β-*compound* is a crystalline powder melting at 136—136·5°; the n-*compound* melts at 158·5—159°. α-*Diphenylmethylpropyl*-1-*phenyl*-ψ-*dithiobiuret* forms silky scales melting at 122·5—123°; the β-*compound* forms pale yellow prisms and melts at 119·5—120°; the n-*compound* melts at 125·5—126° (compare Billeter and Strohl, Abstr., 1888, 364). α-*Diphenylethylpropyl*-1-*phenyl*-ψ-*dithiobiuret* forms bright yellow leaflets melting at 89·5—90°; the β-*compound* melts at 76—76·4° and the n-*compound* at 165·8°. α-*Phenyldimethyl*-1-*phenyl*-ψ-*dithiobiuret* forms colourless needles melting at 91·6—92°; the β-*compound* forms yellow needles and melts at 95°; the n-*compound* melts at 98·8°. α-*Dimethyldipropyl*-1-*phenyl*-ψ-*dithiobiuret* melts at 64·6—65°, the β-*compound* at 48·6—48·8°, and the n-*compound* at 80·5—81°.

Diphenyldiethyl-1-*ethyl*-ψ-*dithiobiuret* melts at 82·6° and the n-*compound* at 158·8°. Hydrogen chloride decomposes it, ethylaniline and ethylthiocarbimide being recognised among the products. *Diphenyldiethyl*-1-*allyl*-ψ-*dithiobiuret*, from allylphenylethylthiocarbimide and phenylethylthiocarbamide chloride, melts at 58·5°; the n-*compound* melts at 143·4—143·6°.

Diphenyldimethyl-1-*benzyl*-ψ-*dithiobiuret* is uncrystallisable; the n-*compound* forms yellow leaflets and melts at 124·8—125°. The n-*diethyl* compound melts at 129·5—130°.

α-*Phenyldimethylethyl*-1-*ethyl*-ψ-*dithiobiuret* forms colourless prisms melting at 66·5—67°; the β-*compound* forms pale yellow, rhombic tablets and melts at 42·8—43°; the n-*compound* forms colourless prisms and melts at 113·5—114°, and is decomposed by hydrogen chloride in chloroform solution, forming ethylaniline, ethylthiocarbimide, and *dimethylxanthogenamide*, melting at 13·8° and boiling at 82·6° under 10 mm. pressure. The latter compound is a secondary product, derived from the action of alcohol on the dimethylthiocarbamide chloride first produced.

β-*Diphenylethyl*-1-*phenyl*-ψ-*dithiobiuret*, NPhEt·CS·S·C(NPh)·NHPh, forms yellow needles melting at 91° and decomposing to form carbon disulphide and triphenylethylguanidine.

Phenyl-α-*naphthylmethylthiocarbamide*, NPhMe·CS·NH·$C_{10}H_7$, forms

colourless crystals melting at 135·5—136°. The β-naphthyl compound is colourless and melts at 124·5—125° (compare Gebhardt, Abstr., 1884, 1320).

Phenyl-α-naphthylethylthiocarbamide forms colourless tablets and melts at 129—129·5°, and the *β-naphthyl* derivative at 128·5—129°.

C. H. D.

Mononitro-derivatives of *p*-Aminophenol. Frédéric Reverdin and Auguste Dresel (*Ber.*, 1904, **37**, 4452—4456; *Bull. Soc. chim.*, 1904, [iii], **31**, 1269—1273).—When the directions given by Hübner, Morse, and Gussefeldt (Abstr., 1882, 505) for the preparation of benzoyl-*p*-aminophenol are followed, *p*-benzoylaminophenyl benzoate is produced, which melts at 233—234°, and on nitration with nitric acid of sp. gr. 1·52, the temperature not being allowed to rise beyond 25°, furnishes a *dinitro*-p-*benzoylaminophenyl benzoate*, which melts at 229° and on saponification yields *dinitro*-p-*aminophenol*: the latter crystallises from water or benzene in red needles with a green sheen and melts at 230—231°; the *acetyl* derivative forms yellow needles and melts at 182°. If nitric acid of sp. gr. 1·48 is employed for the nitration at temperatures from 0° to 10°, there is formed 3-*nitro*-4-*benzoylaminophenyl benzoate*, which exists in two modifications: one form consisting of yellow needles, the other of hard, brown crystals, and both melting at 147°. On saponification with sulphuric acid, this yields 3-nitro-4-aminophenol (m. p. 154°). These results prove that the benzoyl-*p*-aminophenol (m. p. 227·5°), the *m*-nitrobenzoyl-*p*-aminonitrophenol (m. p. 228°), and the *p*-aminonitrophenol (m. p. 183°) described by Hübner (*loc. cit.*) do not exist.

Nitro-derivatives of the aminophenols are best obtained by nitrating products in which the amino- and hydroxyl-groups are both protected, for example, *p*-acetylaminophenyl acetate.

3-Nitro-4-acetylaminophenyl acetate, when treated in the cold with a 40 per cent. solution of sodium hydroxide in water or with sulphuric acid, yields 3-*nitro*-4-*acetylaminophenol*, which crystallises from water in brownish-yellow needles and melts at 218°. p-*Tolylsulphonephenyloxamide* p-*tolylsulphonate* crystallises from benzene in white needles and melts at 169°; the *acetyl* derivative forms yellow, prismatic needles and melts at 150—152°, and the m-*nitro*-derivative, obtained by nitration with nitric acid of sp. gr. 1·48 at 10—15°, yellowish-brown prisms melting at 139°, and on saponification yields *m*-nitro-*p*-aminophenol.

T. A. H.

Constitution of Aromatic Purpuric Acids. VI. The Purpurate Reaction with 2:6-Dinitrophenols. Walther Borsche and E. Böcker (*Ber.*, 1904, **37**, 4388—4397. Compare Abstr., 1904, i, 574).—Whilst picric acid behaves like 2:4-dinitrophenols with respect to purpurate formation, one hydrogen atom being replaced by the cyanogen group and the nitro-group replaced by a NH·OH group, the behaviour of 3:5-dinitro-*p*-cresol and of ethyl 3:5-dinitro-4-hydroxybenzoate is different, since the resulting purpuric

acids contain $1H_2O$ more than was expected. In the latter cases, it is supposed that one of the cyanogen groups introduced is hydrolysed to the $CO\cdot NH_2$ group.

By variation of the experimental conditions, it is possible to obtain, from picric acid, a salt of the acid $C_8H_5O_7N_5$, containing $1H_2O$ more than the *iso*purpurate; further, the normal purpurate, $C_{11}H_7O_6N_4K$, may be obtained from potassium cyanide and ethyl 3 : 5-dinitro-4-hydroxybenzoate.

In the 2 : 6-dinitrophenol purpurates, the two cyanogen groups do not unite with water with the same ease. In purpurate formation, hydrogen cyanide, and not potassium cyanide, is added on, and the cyanogen groups are not introduced successively, but simultaneously.

Potassium p-*cresolpurpurate* (*potassium-3-nitro-5-hydroxylamino-6-carboxylamido-2-cyano-4-hydroxy-1-methylbenzene*),

$$CN\cdot C\lessdot\begin{matrix}CMe{:}C(CO\cdot NH_2)\\C(NO_2)\text{---}C(OK)\end{matrix}\gtrdot C\cdot NH\cdot OH,$$

prepared by warming an alcoholic solution of 3 : 5-dinitro-*p*-cresol with an aqueous solution of potassium cyanide, forms a brown, crystalline powder.

Ammonium-p-*cresolpurpurate*, prepared by decomposing potassium *p*-cresolpurpurate by phosphoric acid and then adding an ethereal solution of ammonia to the ethereal solution of the liberated *p*-cresolpurpuric acid, is a brown, unstable powder. The free *acid* is a dark brown powder which explodes on being heated.

When potassium *p*-cresolpurpurate is heated with aqueous potassium hydroxide, it forms *methyl nitrohydroxylaminopotassoxy*iso*phthalamate monoamide*, $C_9H_9O_8N_3K_2$, which crystallises in needles and, when acted on by phosphoric acid, forms *methyl hydroxylaminonitrohydroxy*iso*phthalic monoamide*, separating in bluish-black crystals.

Ethyl 3-nitro-5-hydroxylamino-2 : 6-cyano-4-potassoxybenzoate,

$$CN\cdot C\lessdot\begin{matrix}C(CO_2Et){:}C(CN)\\C(NO_2)\text{---}C(OK)\end{matrix}\gtrdot C\cdot NH\cdot OH,$$

prepared from ethyl 3 : 5-dinitro-4-hydroxybenzoate and potassium cyanide when the compound, $C_9H_7O_7N_2K,2HCN$, first formed undergoes transformation in a manner not exactly determined, is a "normal" purpurate and is bluish-green.

Ethyl 3-nitro-5-hydroxylamino-6-carboxylamido-2-cyano-4-potassoxybenzoate, $CN\cdot C\lessdot\begin{matrix}C(CO_2Et){:}C(CO\cdot NH_2)\\C(NO_2)\text{------}C(OK)\end{matrix}\gtrdot C\cdot NH\cdot OH$, prepared by the action of ethyl 3 : 5-dinitro-4-hydroxybenzoate on potassium cyanide at a higher temperature than in the preceding case, separates from water in brick-red needles. The corresponding *ammonium* salt has similar physical properties.

Potassium iso*purpurate* (*1 : 3-dinitro-5-hydroxylamino-2 : 6-cyano-4-potassoxybenzene*), $CN\cdot C\lessdot\begin{matrix}C(NO_2){:}C(CN)\\C(NO_2)\cdot C(OK)\end{matrix}\gtrdot C\cdot NH\cdot OH$, prepared from picric acid and potassium cyanide, forms a dark red mass, as also does the *ammonium* salt. The *free* acid is dark violet.

1 : 3-*Dinitro-5-hydroxylamino-6-carboxylamido-2-cyano-4-potassoxybenzene*, prepared from picric acid and potassium cyanide at 50—60°, is a dark coloured, explosive compound. A. McK.

Symmetrical Trinitroxylenol. EDMUND KNECHT (*Ber.*, 1904, **37**, 4193).—*s*-Trinitroxylenol (Knecht and Hibbert, Abstr., 1904, i, 871) has been previously described by Blanksma (Abstr., 1902, i, 286).

C. H. D.

Occurrence of a Dihydrocuminol in Ginger Grass Oil. HEINRICH WALBAUM and O. HÜTHIG (*Chem. Zeit.*, 1904, **28**, 1143).—The dihydrocuminol, $C_{10}H_{16}O$, obtained from Ginger grass oil, boils at 228—229° under 755 mm. and at 94·5—96° under 4—5 mm. pressure; it has the sp. gr. 0·9536 at 15°, α_D + 12°5′ (length of tube not stated), and n_D 1·49761 at 20°. When oxidised by chromic acid, it forms the aldehyde, $C_{10}H_{14}O$, which, when oxidised by silver oxide, forms the acid, $C_{10}H_{14}O_2$, which is probably dihydrocuminic acid. When the latter acid is oxidised by dilute nitric acid, it forms cuminic acid, whilst concentrated nitric acid converts it into 3-nitrocuminic acid.

When the dihydrocuminol is warmed with a concentrated solution of formic acid, cymene is formed.

A. McK.

Geometrical Isomerism of Derivatives of Diphenylethylene. RICHARD STOERMER and M. SIMON (*Ber.*, 1904, **37**, 4163—4168).—Geometrical isomerism is possible in derivatives of diphenylethylene when one hydrogen atom of the methylene group and one atom in a benzene nucleus are replaced. In the following, the compound with the higher melting point, which is also the less soluble, is designated the α-, the other the β-isomeride. The actual configuration has not been determined.

Phenyl-*o*-anisylbromoethylene, $CHBr\colon CPh\cdot C_6H_4\cdot OMe$ (O. Kippe, *Diss. Rostock*, 1904), may be separated into two fractions by crystallisation from alcohol. The *α-compound* forms long needles melting at 78·5°; the *β-compound* forms indefinite crystals and melts at 56·5°. Sunlight slowly converts the alcoholic or ethereal solution of the α- into the β-compound, but the transition could not be effected by any other means.

*Phenyl-*o*-anisyldichloroethylene*, prepared by passing chlorine into a solution of phenyl-*o*-anisylethylene in carbon disulphide, forms small, highly refractive cubes and melts at 90°. On heating under reduced pressure or with alcoholic sodium hydroxide, the *monochloro*-compound is obtained and may be separated by crystallisation. The *α-compound* forms long, glistening prisms and melts at 71·5°; the *β-compound* forms short crystals melting at 50·5°. Sunlight converts the α- into the β-form.

Phenyl p-*anisylethylene*, prepared from phenyl-*p*-anisyl ketone and magnesium methyl iodide, forms silvery leaflets and melts at 75°. The *α-bromo*-derivative melts at 82·5° and the β-derivative at 52°.

*α-Phenyl-*p-*anisylchloroethylene* melts at 59—60° and the *β-compound* at 26—28°.

α-Phenyl-α-naphthylbromoethylene melts at 71—72° and the *β-compound* at 54°.

p-*Bromodiphenylethylene*, prepared from *p*-bromobenzophenone and

magnesium methyl bromide, boils at 199—201° under 19 mm. pressure. α-p-*Bromodiphenylbromoethylene* forms glistening prisms and melts at 107°; the β-compound melts at 35°. C. H. D.

Conversion of Nitronaphthalenes into Nitroso-derivatives of Naphthol. Carl Graebe (*Annalen*, 1904, **335**, 139—144. Compare Abstr., 1900, i, 24; Friedländer, Abstr., 1900, i, 150).—1 : 6-*Dinitro-β-naphthyl methyl ether*, $C_{11}H_8O_5N_2$, is best prepared by the action of methyl sulphate on the potassium compound; it crystallises in brown needles, melts at 202°, and yields 1 : 6-dinitro-β-naphthylamine when heated at 155—160° with alcoholic ammonia.

When treated with sulphuric acid containing 15—17 per cent. of anhydride at 40—50°, 1 : 6-dinitronaphthalene yields a *nitronitrosonaphthol*, which crystallises in brown needles, decomposes above 200°, dissolves in concentrated sulphuric acid to a yellow, in aqueous alkali hydroxides to reddish-brown solutions, yields 4-nitrophthalic acid when oxidised with potassium permanganate, and is probably 7-nitro-4-nitroso-α-naphthol.

When treated with fuming sulphuric acid, 1 : 3-dinitronaphthalene yields a *product* which is insoluble in water, but easily soluble in aqueous alkali hydroxides. G. Y.

5 : 4- and 8 : 4-Nitronitroso-α-naphthols. Carl Graebe and A. Oeser (*Annalen*, 1904, **335**, 145—156. Compare foregoing abstract). —5-Nitro-4-nitroso-α-naphthol (Abstr., 1900, i, 24, 150) crystallises in yellow needles, decomposes at 250—260°, is insoluble in water, but easily soluble in alcohol, glacial acetic acid, or aqueous alkali hydroxides, and dissolves in concentrated sulphuric acid to a yellow solution; a yellow, crystalline precipitate is formed on addition of lead acetate to a solution of the nitrosonitronaphthol in aqueous ammonia. With dilute nitric acid at the ordinary temperature, it is oxidised to naphthapicric acid; with alkaline potassium permanganate, to 3-nitrophthalic acid.

8-*Aminonaphthaquinol* (8-*amino*-1 : 4-*dihydroxynaphthalene*) *hydrochloride*, obtained by reduction of 5-nitro-4-nitroso-α-naphthol with tin and hydrochloric acid, crystallises in colourless needles and gives a red, crystalline *precipitate* when treated with ferric chloride.

8-Acetylamino-1 : 4-naphthaquinone, obtained by oxidation of 8-acetylaminonaphthaquinol, crystallises in leaflets and melts at 162°.

4 : 5-Diamino-α-naphthol hydrochloride is obtained by reduction of 5-nitro-4-nitroso-α-naphthol with stannous chloride at the ordinary temperature.

8-Nitro-4-nitroso-α-naphthol, obtained from 1 : 5-dinitronaphthalene, forms yellow crystals and decomposes at 235—240°; the *barium* derivative, $(C_{10}H_5O_4N_2)_2Ba,3H_2O$, forms yellow crystals.

4 : 8-Dinitro-α-naphthol melts at 235° (compare Abstr., 1900, i, 150); the *potassium* and *ammonium* derivatives are easily soluble in boiling water; the *silver* derivative is red; the *ethyl* ether crystallises in brown needles and melts at 115°. G. Y.

Action of Bromine and Chlorine on Phenols: Substitution Products; ψ-Bromides and ψ-Chlorides. XII. ψ-Bromo-*p*-dihydroxystilbene, Stilbenequinone, and their Products. THEODOR ZINCKE and S. MÜNCH (*Annalen*, 1904, **335**, 157—191. Compare Abstr., 1902, i, 178, 179).—*Di*-p-*hydroxystilbene ψ-dibromide*,

$OH\cdot C_6H_4\cdot CHBr\cdot CHBr\cdot C_6H_4\cdot OH$ or $C_6H_5O\cdot CHBr\cdot CHBr\cdot C_6H_5O$, is obtained by the action of bromine on di-*p*-hydroxystilbene in ethereal solution cooled by a freezing mixture. It crystallises in small leaflets, or from acetone in needles, decomposes when heated, loses bromine with regeneration of dihydroxystilbene on prolonged boiling in acetone, gives an intense red coloration and separation of a green substance when treated with aqueous sodium hydroxide, and yields stilbenequinone when acted on by water or sodium carbonate solution.

Stilbenequinone, $C_6H_4O{:}CH\cdot CH{:}C_6H_4O$, is prepared by shaking an ethereal suspension of the ψ-dibromide with aqueous sodium acetate. It crystallises in small, red needles, is unstable when moist, reacts easily with alcohol, acetic acid, and acetic anhydride, and is reduced by stannous chloride to di-*p*-hydroxystilbene.

In contact with acetone, stilbenequinone yields a white polymeride (?) which, with concentrated sulphuric acid, regenerates the quinone.

Di-p-*hydroxystilbene-ψ-dichloride*, formed by the action of hydrogen chloride on stilbenequinone in glacial acetic acid solution, crystallises in thick needles and resembles the ψ-dibromide.

Stilbenequinhydrone, $O{<}{\begin{matrix}C_6H_4\text{———}CH{:}CH\text{———}C_6H_4\\ C_6H_4(OH){:}CH\cdot CH{:}C_6H_4(OH)\end{matrix}}{>}O$, formed by the action of stilbenequinone on di-*p*-hydroxystilbene, by the action of the ψ-dibromide on di-*p*-hydroxystilbene in presence of sodium acetate, or by oxidation of di-*p*-hydroxystilbene with ferric chloride, crystallises in small, green needles which are violet by transmitted light, is sparingly soluble, and is converted into di-*p*-hydroxystilbene on prolonged treatment with water.

The green *sodium* derivative of stilbenequinhydrone is formed by the action of bromine water on an alkaline solution of di-*p*-hydroxystilbene or by the action of aqueous sodium hydroxide on stilbenequinone or the ψ-dibromide.

The action of methyl alcohol on the ψ-dibromide leads to the formation of three dimethoxy-derivatives.

The *quinone*, $C_2H_2(OMe)_2\left(CH{<}{\begin{matrix}CH{:}CH\\ CH{:}CH\end{matrix}}{>}CO\right)_2$, formed by the action of methyl alcohol on the ψ-dibromide in ethereal solution, crystallises in small, colourless needles, yields stilbenequinone when dried over sulphuric acid, and is easily soluble in aqueous alkali hydroxides.

Di-p-*hydroxyhydrobenzoin dimethyl ether*, $C_2H_2(OMe)_2(C_6H_4\cdot OH)_2$, obtained on the addition of an acid to the alkaline solution of the quinone form, crystallises in large plates and melts and decomposes at 220°; the *diacetyl* derivative crystallises in short prisms and melts at 153°.

Di-p-*hydroxy*iso*hydrobenzoin*, formed along with the hydrobenzoin derivative by the action of methyl-alcoholic potassium hydroxide on the ψ-dibromide, crystallises in thick needles and melts at 205° the

diacetyl derivative crystallises in colourless needles, melts at 91°, and is more soluble in benzene than the isomeride.

Di-p-acetoxystilbene dibromide, $C_2H_2Br_2(C_6H_4\cdot OAc)_2$, obtained by the action of bromine on di-*p*-acetoxystilbene, by acetylation of the ψ-dibromide with acetic anhydride, and by addition of acetyl bromide to stilbenequinone, occurs in two forms. The hydrobenzoin form crystallises in colourless needles, melts, with evolution of hydrogen bromide, at 215°, slowly decomposes at the ordinary temperature, and when treated with concentrated sulphuric acid yields acetyl bromide and stilbenequinone. The *iso*hydrobenzoin derivative crystallises in thick needles, melts at 170°, and is more soluble than its isomeride. If heated carefully to its melting point, the *iso*hydrobenzoin compound undergoes isomeric change into the higher melting modification.

Di-p-acetoxystilbene dichloride is obtained in two modifications: the one crystallises in long, colourless needles and melts and decomposes at 220°; the other crystallises from methyl alcohol in needles, from benzene in prisms containing benzene of crystallisation, melts at 132°, and is converted into the higher melting modification when heated with glacial acetic acid and hydrogen chloride at 100°, or when heated above its melting point until evolution of hydrogen chloride commences. When treated with methyl alcoholic potassium hydroxide, both dichlorides yield the dimethyl ether of dihydroxyhydrobenzoin and di-*p*-hydroxytolane. With alkali hydroxides in acetone solution, the dichlorides yield dihydroxystilbene.

Di-p-acetoxybromostilbene, $OAc\cdot C_6H_4\cdot CH\colon CBr\cdot C_6H_4\cdot OAc$, obtained by heating di-*p*-acetoxystilbene dibromide (m. p. 215°) until completely melted, crystallises in colourless needles, melts at 126—127°, and yields di-*p*-hydroxytolane when treated with alcoholic potassium hydroxide. *Di-p-acetoxychlorostilbene* crystallises in long leaflets and melts at 125—126° to an opaque, doubly-refracting liquid, which becomes clear at 138°.

Di-p-hydroxytolane, $OH\cdot C_6H_4\cdot C\vdots C\cdot C_6H_4\cdot OH$, crystallises in needles and melts at 220—225°; the *diacetyl* derivative crystallises in long needles and melts at 198°. When treated with concentrated sulphuric acid, dihydroxytolane and its diacetyl derivative yield an intensely red, crystalline *substance* of a quinonoid nature, which dissolves in glacial acetic acid to a red, in aqueous alkali hydroxides to a violet, solution.

The action of acetic anhydride and sodium acetate on di-*p*-acetoxyhydrobenzoin dibromide leads to the formation of (1) the *tetra-acetyl* compound, $C_2H_2(OAc)_2(C_6H_4\cdot OAc)_2$, which is obtained in two modifications; the one crystallising in thick needles, containing benzene of crystallisation, and melting at 172—173°; the other crystallising in slender needles and melting at 124—125°; and (2) *dihydroxystilbene diacetate*, which crystallises in needles and melts at 211—212°. G. Y.

Mixed Phenolic Sulphides. F. Taboury (*Bull. Soc. chim.*, 1904, [iii], **31**, 1183—1188. Compare Abstr., 1903, i, 748).—When an alkyl haloid reacts with the compounds obtained by the interaction of sulphur with magnesium alkyl haloids (*loc. cit.*), mixed sulphides are produced. *Phenyl benzyl sulphide*, $CH_2Ph\cdot S\cdot Ph$, crystallises in white

lamellæ and melts at 40—41°; its solution in sulphuric acid becomes orange on warming. p-*Bromophenyl methyl sulphide* melts at 32°. p-*Bromophenyl benzyl sulphide* forms small, white crystals, melts at 64—65°, and is soluble in alcohol and ether, less so in light petroleum. p-*Chlorophenyl benzyl sulphide* crystallises in small, white lamellæ and melts at 52—53°. α-*Naphthyl methyl sulphide* is a colourless liquid and boils at 166—168° under 20 mm. pressure. *Benzyl α-naphthyl sulphide* crystallises from a mixture of alcohol and water in white lamellæ and melts at 78—80°. T. A. H.

Aminoalcohols. Synthetic at Ephedrines. ERNEST FOURNEAU (*J. Pharm. Chim.*, 1904, [vi], **20**, 481—491).—Four isomerides of ephedrine and ψ-ephedrine have been prepared, one of which is most probably the racemic modification of ψ-ephedrine, but has not been resolved into its optically active components. The substituted amino-alcohols described in the paper were prepared by the action of methylamine or dimethylamine on the chloro- or iodo-hydrins of the corresponding unsaturated hydrocarbons.

Phenylmethylaminodimethylcarbinol, $NHMe\cdot CH_2\cdot CMePh\cdot OH$, is a colourless, syrupy liquid, boiling at 137° under 33 mm. pressure, slightly soluble in cold, almost insoluble in warm water. The *hydrochloride* and *oxalate* melt at 153° and 158° respectively, and the *aurichloride* decomposes at 148°. The *dibenzoyl* derivative forms brilliant prisms melting at 122°.

Phenylmethylaminoethylcarbinol, $NHMe\cdot CHMe\cdot CHPh\cdot OH$, forms colourless prisms melting at 60°, and boils at 155—156° under 31 mm. pressure. The odour is that of ψ-ephedrine. It is easily soluble in ether and in alcohol, and dissolves in about its own bulk of water, probably forming a hydrate, which is unstable on warming.

The *hydrochloride* and the *dibenzoyl* derivative melt at 178° and 92° respectively.

Phenyldimethylaminoethylcarbinol, $NMe_2\cdot CHMe\cdot CHPh\cdot OH$, forms prismatic needles melting at 47° and boils at 151—152° under 31 mm. pressure. The *hydrochloride, picrate*, and *methiodide* melt at 180°, 80°, and 225° respectively. The *benzoyl* derivative, melting at 108°, has an intense anæsthetic action.

Benzylmethylaminomethylcarbinol, $NHMe\cdot CH_2\cdot CH(CH_2Ph)\cdot OH$, boils at 148° under 22 mm., or at 169° under 40 mm. pressure. Neither the base nor its salts are crystallisable. The *methiodide* and the *dibenzoyl* derivative melt at 148° and 42—43° respectively.

Benzyldimethylaminomethylcarbinol is a liquid boiling at 143° under 22 mm. pressure and yielding an *aurichloride* melting at 122°. The liquid *benzoyl* derivative has a bitter taste and anæsthetic action, and forms a *hydrochloride* melting at 165°.

γ-*Methylamino-β-phenylpropyl alcohol*, $NHMe\cdot CH_2\cdot CHPh\cdot CH_2\cdot OH$, boiling at 145° under 24 mm. pressure, is a liquid, as also are its salts. The corresponding *dimethylamino*-compound is liquid and boils at 136° under 24 mm. or at 153° under 42 mm. pressure. The *hydrochloride*, which is hygroscopic, *aurichloride*, and *methiodide* melt at 288°, 126—127°, and 148° respectively. The hydrochloride of the *benzoyl*

derivative has local anæsthetic action, melts at 175°, and gives a *mercurichloride* melting at 141°. G. D. L.

Secondary Phenylnitroethanol. M. Holleman (*Rec. Trav. Chim.*, 1904, **23**, 298—300).—Bouveault and Wahl have shown (Abstr., 1902, i, 682) that when benzaldehyde is condensed with nitromethane in presence of sodium methoxide the first product is the compound OH·CHPh·CH⁚NO·ONa, which, on addition of sulphuric acid, is decomposed forming the corresponding secondary nitro-alcohol, which is at the same time partially dehydrated furnishing β-nitrostyrene (compare Thiele and Haeckel, Abstr., 1903, i, 160). The nitro-alcohol can be obtained pure by the addition of acetic acid to the reaction mixture in place of sulphuric acid; it is a bright yellow, viscous liquid, which, when slightly warmed, turns brown and is partially changed into β-nitrostyrene. On oxidation with potassium dichromate and sulphuric acid, it yields α-nitroacetophenone.

T. A. H.

***p*-Methoxyphenylethylcarbinol.** Carl Hell and Alexander Hofmann (*Ber.*, 1904, **37**, 4188—4193).—Phenylethylcarbinols prepared by Grignard's synthesis, and containing a *p*-methoxy-group, have been found to be unstable, losing water on distillation to form alkylene derivatives (Abstr., 1904, i, 241, 242). On the other hand, *p*-methoxyphenylethylcarbinol, prepared by the reduction of propionylanisole, has been described by Klages (Abstr., 1902, i, 609) as being volatile without decomposition. The authors have prepared this compound from anisaldehyde and magnesium ethyl bromide, and find that on distillation under reduced pressure partial decomposition takes place, anethole, $OMe\cdot C_6H_4\cdot CH⁚CHMe$, being formed. After twice distilling under the ordinary pressure, pure anethole is obtained. The decomposition takes place slowly even in the cold. It was not found possible to prepare Klage's phenylurethane derivative, the carbinol yielding only *s*-diphenylcarbamide with phenylcarbimide. C. H. D.

Intramolecular Atomic Rearrangements in Benzpinacones. P. J. Montagne (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, **7**, 271—275).—When 4 : 4′ : 4″ : 4‴-tetrachlorobenzpinacone, obtained by reduction of 4 : 4′-dichlorobenzophenone, is heated with acetyl chloride, tetrachlorobenzpinacolin is formed, which, when boiled with alcoholic potassium hydroxide, forms trichlorotriphenylmethane and *p*-chlorobenzoic acid. Since the trichlorotriphenylmethane obtained is identical with the product obtained from *p*-leucaniline, it is concluded that the intermediate product, demanded by Nef's hypothesis as applied to the formation of a pinacoline from a pinacone, is an impossibility.

In the transformation of $\alpha\beta$-glycols into aldehydes, an intramolecular rearrangement occurs, which cannot be explained by any normal intermediate reaction. It has not, however, been decided as to whether this atomic migration takes place with the $\alpha\beta$-glycols themselves, or whether the oxides are formed first and then undergo intramolecular rearrangement. A. McK.

Derivatives of Amino-acids. Max Siegfried (*Zeit. physiol. Chem.*, 1904, **43**, 68—71).—Amino-acids yield characteristic derivatives when their alkaline solutions are thoroughly shaken with ethereal solutions of 4-nitrotoluene-2-sulphonic chloride.

4-*Nitrotoluene-2-sulphoglycine*, $NO_2\cdot C_6H_3Me\cdot SO_2\cdot NH\cdot CH_2\cdot CO_2H$, crystallises from hot water in long needles or large, thin plates melting at 180° (corr.). The *barium* salt crystallises from water in long prisms.

r-4-*Nitrotoluene-2-sulphoalanine*,

$$NO_2\cdot C_6H_3Me\cdot SO_2\cdot NH\cdot CHMe\cdot CO_2H,$$

crystallises in slender needles melting at 96°. One part of the acid dissolves in 690 of water at 12°.

r-4-*Nitrotoluene-2-sulphoglutamic acid*,

$$NO_2\cdot C_6H_3Me\cdot SO_2\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot CH_2\cdot CO_2H,$$

crystallises in long, slender needles, melts at 160—161° (corr.), and readily forms supersaturated solutions. The *barium* salt crystallises from water in colourless prisms. J. J. S.

Nitriles of Hydroxy- and Amino-carboxylic Acids. Hans Th. Bucherer (*Ber.*, 1904, **37**, 4510—4513. Compare Knoevenagel, Abstr., 1904, i, 981, 989, 994, 1024, 1027, 1028).—A claim for priority. C. H. D.

Action of an Ammoniacal Solution of Silver Oxide on Salicylic Acid and Salicylaldehyde. Heinrich Brunner (*Chem. Zeit.*, 1904, **28**, 1123—1124. Compare Abstr., 1902, i, 452).—*iso*-Salicylic acid, previously described (*loc. cit.*), does not exist. A nitro-compound is formed when an ammoniacal solution of silver oxide acts on salicylic acid. A. McK.

A New Preparation of Alphylthiosalicylic Acids. Irma Goldberg (*Ber.*, 1904, **37**, 4526—4527).—The sodium salt of thiophenol reacts with potassium *o*-chlorobenzoate at 220—230° in presence of a small quantity of copper to form phenylthiosalicylic acid: $C_6H_4Cl\cdot CO_2K + C_6H_5\cdot SNa = CO_2K\cdot C_6H_4\cdot SPh + NaCl$. The product is identical with the acid obtained by Graebe and Schultess (Abstr., 1891, 1058) from thiophenol and *o*-diazobenzoic acid chloride.

p-*Tolylthiosalicylic acid*, $CO_2H\cdot C_6H_4\cdot S\cdot C_6H_4Me$, from *p*-thiocresol, melts at 215—216° (corr.) and dissolves readily in alcohol, benzene, acetic acid, or ether, very sparingly in cold water or light petroleum. The solution in concentrated sulphuric acid is yellow, and shows a green fluorescence on warming (formation of a thioxanthone).

β-Naphthylthiosalicylic acid, $CO_2H\cdot C_6H_4\cdot S\cdot C_{10}H_7$, from β-thionaphthol, crystallises from alcohol in glistening, white leaflets and melts at 200—201° (corr.). The solution in concentrated sulphuric acid is yellow, with slight green fluorescence. C. H. D.

Reduction Products of Ethyl 2 : 4-Dinitrophenylacetoacetate. Arnold Reissert and Hans Heller (*Ber.*, 1904, **37**, 4364—4379).—Ethyl 2 : 4-dinitrophenylacetoacetate (compare Heckmann, Abstr.,

1884, 178) is conveniently prepared by the interaction of ethyl sodioacetoacetate with chlorodinitrobenzene in cold alcoholic solution, the mixture being left for two weeks. When reduced with stannous chloride under special experimental conditions, a mixture is obtained of 1 part of *ethyl aminomethylindolecarboxylate* and 5 parts of the ester-amide next described. *Ethyl* 2 : 4-*diaminophenylacetoacetyl*-2 : 4-*diaminophenylacetoacetate*,

$$C_6H_3(NH_2)_2\cdot CHAc\cdot CO\cdot NH\cdot C_6H_3(NH_2)\cdot CHAc\cdot CO_2Et,$$

crystallises from alcohol in colourless needles, turns brown at 212°, and melts and decomposes at 217·5°; it gives a green coloration with ferric chloride. The *hydrochloride* crystallises in plates, the *sulphate* in glistening platelets, the *metallic* salts not being well characterised. The *penta-acetyl* derivative, $C_{21}H_{21}O_5N_4Ac_5$, crystallises in colourless needles melting at 167°; the *diacetyl* derivative, which is prepared in the form of the sodium salt by warming the penta-acetyl derivative with dilute sodium hydroxide, crystallises in colourless, granular crystals which decompose at 249—250°.

The *tribenzoyl* derivative, prepared by benzoylating in presence of an alkaline hydroxide at 0°, melts at 167·5°; on prolonged boiling with alcoholic alkali, the *dibenzoyl* derivative is formed, crystallising from alcohol in colourless plates melting at 201·5°. The *tetrazo*-derivative of the ester-amide, $C_{22}H_{20}O_5N(N_2Cl)_2\cdot NH_2,HCl,2H_2O$, crystallises in glistening, green plates and couples with β-naphthol to form a dark red and with resorcinol to form a bright red dye.

2′ : 4′-*Diaminophenylacetoacetyl*-6-*amino*-2-*methylindole*,

$$C_6H_3(NH_2)_2\cdot CHAc\cdot CO\cdot N{<}\begin{matrix}C_6H_3(NH_2)\\ \overline{CMe}\end{matrix}{>}CH,$$

prepared by the action of 30 per cent. sodium hydroxide in sealed tubes at 100° on the ester-amide, forms bright yellow crystals, which rapidly become blue in the air and decompose with great violence at 142·5°. The *tribenzoyl* derivative crystallises in colourless crystals decomposing at 138°. *Ethyl* 6-*amino*-2-*methylindole*-3-*carboxylate* is formed when the ester-amide is heated at 230—240°; it crystallises from alcohol in colourless, glistening plates melting at 185°; the *hydrochloride* crystallises in plates, the *acetate* in rhombohedra which sublime at 340° without decomposing.

6-*Amino*-2-*methylindole*, prepared by the action of sulphuric acid on the foregoing compound, crystallises from alcohol in well formed prisms melting at 82°; these decompose very rapidly even in a vacuum. The *picrate* crystallises in dark yellow plates melting at 192°; the *benzoyl* compound forms colourless plates and melts at 209°; the *acetyl* derivative melts at 180·5°. The structure of ethyl 6-amino-2-methylindolecarboxylate was confirmed by the replacement of the amino-group through the diazo-reaction and the hydrazine-groups by hydrogen, when the ethyl methylindole-3-carboxylate described by Nef was obtained (Abstr., 1892, 140). E. F. A.

Chrysodiphenic Acid. [2′-Phenylnaphthalene-1 : 2′-dicarboxylic Acid.] Carl Graebe and Robert Gnehm, jun. (*Annalen*, 1904, **335**, 113—121. Compare Abstr., 1902, i, 679).—When strongly heated, chrysodiphenic acid yields chrysoketone and traces of β-phenyl-

naphthalene; the *silver* salt, $C_{18}H_{10}O_4Ag_2$, is obtained as a colourless precipitate.

The *methyl hydrogen* ester, $CO_2H{\cdot}C_{10}H_6{\cdot}C_6H_4{\cdot}CO_2Me$, formed by the action of methyl alcohol and hydrogen chloride on the acid or by the action of methyl alcohol on the anhydride, crystallises in prisms, melts at 124°, and forms the *silver* salt, $C_{19}H_{13}O_4Ag$. The isomeric *methyl hydrogen* ester, $CO_2Me{\cdot}C_{10}H_6{\cdot}C_6H_4{\cdot}CO_2H$, formed by partial hydrolysis of the dimethyl ester, melts at 171·5°. The *dimethyl* ester crystallises in plates and melts at 90°. The anhydride,

$$\begin{array}{l} C_{10}H_6{\cdot}CO \\ | \\ C_6H_4{-}CO \end{array}\!\!>O,$$

crystallises in colourless needles, melts at 146°, when strongly heated yields chrysoketone, and, with ammonia, forms the amic acid,

$$CO_2H{\cdot}C_{10}H_6{\cdot}C_6H_4{\cdot}CO{\cdot}NH_2,$$

which melts at 220°. Chrysoketonecarboxylic acid, which, along with a small amount of its isomeride, is formed by the action of sulphuric acid on chrysodiphenic acid, melts at 283°, is identical with Graebe and Hönigsberger's acid (Abstr., 1900, i, 506), and yields only traces of an ester when heated on the water-bath with methyl alcohol and hydrogen chloride. It has probably the constitution

$$CO<\begin{array}{l} C_{10}H_5{\cdot}CO_2H \\ | \\ C_6H_4 \end{array},$$

but when heated with zinc dust it yields chrysofluorene,

$$C_6H_4<\begin{array}{l} CH{:}C{\cdot}CH_2 \\ \quad\;\;| \\ CH{:}C{-\!-\!-\!-} \end{array}\!\!>C_6H_4.$$

G. Y.

Condensing Action of Organic Bases. Emil Knoevenagel (*Ber.*, 1904, **37**, 4461—4463).—A *résumé* of the literature on the condensations of aldehydes, ketones, esters, and keto-esters with ammonia, or primary or secondary bases, and an introduction to the following papers.

G. Y.

Condensing Action of Organic Bases. Emil Knoevenagel and Siegbert Mottek (*Ber.*, 1904, **37**, 4464—4476).—In presence of diethylamine, ethyl cyanoacetate and methyl fumarate react at the ordinary temperature, forming ethyl dimethyl cyanotricarballylate, $CO_2Me{\cdot}CH_2{\cdot}CH(CO_2Me){\cdot}CH(CN){\cdot}CO_2Et$, which is a yellow oil, distils at 190—210° under 16 mm. pressure, and when hydrolysed with hydrochloric acid yields tricarballylic acid.

In presence of diethylamine and ethylamine, or, with poorer yield, piperidine, methyl fumarate and ethyl malonate form dimethyl diethyl propanetetracarboxylate, which boils at 198—210° under 18 mm. pressure and is hydrolysed by hydrochloric acid to tricarballylic acid.

Carvone combines with ethyl cyanoacetate, in presence of diethylamine or piperidine, to form *ethyl dihydrocarvonylcyanoacetate*,

$$CH_2{:}CMe{\cdot}C_6H_7MeO{\cdot}CH(CN){\cdot}CO_2Et,$$

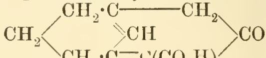
which is a yellow, viscid oil, boils at 150—151° under about 1 mm. pressure, has a bitter, unpleasant flavour, and is almost insoluble in water. The *oxime*, $C_{15}H_{22}O_3N_2$, crystallises in matted needles, melts at 109—111°, or, after recrystallisation from 70 per cent. alcohol, at

119—121°. Hydrolysis of the ester leads to the formation of *dihydrocarvonylacetic acid*, $CH_2:CMe\cdot C_6H_7MeO\cdot CH_2\cdot CO_2H$, which is a brown, viscid oil; it decomposes on distillation under reduced pressure and yields a flocculent *silver* salt, $C_{12}H_{17}O_3Ag$.

*Ethyl 1-methyl*cyclo*hexenylidene-3-cyanoacetate*,

$$C_6H_7Me:C(CN)\cdot CO_2Et,$$

formed by the action of ethyl cyanoacetate on methyl*cyclo*hexenone in presence of diethylamine or of piperidine, melts at 55—57° to a yellow oil, which distils at 178—190° under 12 mm. pressure. The ester is stable towards acids, but is easily attacked by alkalis; it is hydrolysed by 10—15 per cent. potassium hydroxide solution to methyl*cyclo*hexenone and malonic acid; hydrolysis with dilute sodium carbonate or 2—5 per cent. potassium hydroxide solution leads to the formation of the *acid*,



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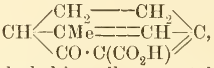
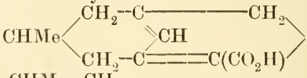


which separates from alcohol in yellow crystals, melts at 147—148·5°, and yields methyl*cyclo*hexenone and potassium malonate when boiled with 10 per cent. potassium hydroxide solution. The *ammonium*, *ferric*, and *silver*, $C_{10}H_9O_3Ag$, salts are described; two *methyl* esters, $C_{11}H_{12}O_3$, melting at 37—39° and 64—66° respectively, are obtained by the action of methyl iodide on the silver salt.

*Ethyl 1 : 5-dimethyl*cyclo*hexenylidene-3-cyanoacetate*,

$$C_6H_6Me_2:C(CN)\cdot CO_2Et,$$

obtained by the action of ethyl cyanoacetate on dimethyl*cyclo*hexenone in the presence of diethylamine, separates from alcohol in yellow crystals, melts at 57—58°, boils at 192—195° under 16 mm. pressure, and is stable towards acids. When boiled with 10 per cent. potassium hydroxide solution, the ester yields potassium malonate and dimethyl*cyclo*hexenone. Hydrolysis of the ester with dilute sodium carbonate or very dilute potassium hydroxide solution leads to the formation of the *acid*,



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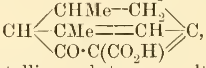


which is a yellow, crystalline substance, melts at 135—136°, and is easily soluble in alcohol, ether, or chloroform, but is insoluble in water. The *ammonium* salt melts and decomposes at 164°; the *silver* salt, $C_{11}H_{11}O_3Ag$, is obtained as a white powder. G. Y.

Condensation of Vanillin with Ethyl Acetoacetate and its Analogues. EMIL KNOEVENAGEL and FRIEDRICH ALBERT (*Ber.*, 1904, **37**, 4476—4482).—Vanillin reacts with 1 or 2 mols. of ethyl acetoacetate, or 1 or 2 mols. of acetylacetone, or with ethyl malonate in presence of diethylamine, or more energetically in presence of

piperidine, to form the following condensation products. *Ethyl vanillylideneacetoacetate*, $C_{14}H_{16}O_5$, crystallises from dilute alcohol, melts at 120—121°, and is soluble in aqueous alkali hydroxides, but insoluble in acids. When warmed with hydroxylamine hydrochloride in alcoholic solution, it forms 5-*keto*-3-*methyl*-4-*vanillylidene*-4 : 5-*dihydro*-iso*oxazole*, $\left.\begin{matrix}O\cdot CO\text{--}\\ | \\ N{:}CMe\end{matrix}\right\rangle C{:}CH\cdot C_6H_3(OMe)\cdot OH$, which melts at 220° and is soluble in aqueous alkali hydroxides, but not in acids.

Ethyl vanillylidenebisacetoacetate, $C_{20}H_{26}O_8$, melts at 163—164° and decomposes when heated above its melting point. The *oxime*, $C_{20}H_{27}O_8N$, forms white crystals and melts at 198—200°, or, after recrystallisation from alcohol, at 210—220°.

Hydrolysis of the ester with dilute alkali hydroxides leads to the formation of *vanillylidenebisacetoacetic acid*, $C_{16}H_{18}O_8$, which melts and decomposes at 127—128°. *Ethyl* 1-*keto*-5-*methyl*-3-p-*hydroxy*-m-*methoxyphenyl*-1 : 2 : 3 : 4-*tetrahydrobenzene*-2 : 4-*dicarboxylate*,

$$OH\cdot C_6H_3(OMe)\cdot C_6H_4OMe(CO_2Et)_2,$$

obtained by the action of hydrogen chloride on the ester in alcoholic solution, crystallises in white needles and melts at 146—147°.

Vanillylideneacetylacetone, $C_{13}H_{14}O_4$, crystallises in thin, yellow needles and melts at 135°. Vanillylidenebisacetylacetone, $C_{18}H_{22}O_6$, crystallises in slender, white needles and melts, when crude, at 150—151°, or, after recrystallisation, at 170—171°. The action of hydroxylamine hydrochloride on vanillylidenebisacetylacetone in dilute alcoholic solution leads to the formation of the oxime of 1-*keto*-2 : 4-*diacetyl*-5-*methyl*-3-p-*hydroxy*-m-*methoxy*-*phenyl*-1 : 2 : 3 : 4-*tetrahydrobenzene*, $OH\cdot C_6H_3(OMe)\cdot C_6H_4MeAc_2{:}N\cdot OH$, which melts at 223—224°.

Ethyl vanillylidenemalonate, $C_{15}H_{18}O_6$, melts at 110°. *Vanillylidenemalonic acid* melts at 212°. G. Y.

Condensation of Cinnamaldehyde with Ethyl Malonate and Acetylacetone. EMIL KNOEVENAGEL and ALBERT HERZ (*Ber.*, 1904, **37**, 4483—4484).—*Ethyl cinnamylidenebismalonate*, $C_{23}H_{30}O_8$, obtained by the condensation of cinnamaldehyde with ethyl malonate in presence of piperidine, melts at 36° to a mobile oil which boils at 218° under 9 mm. pressure.

Cinnamylideneacetylacetone, $C_{14}H_{14}O_2$, forms yellow crystals, melts at 102·5°, and boils at 191° under 17 mm., or, almost without decomposition, at 304° under the ordinary pressure. G. Y.

Condensation of β-Hydroxy-α-naphthaldehyde with Ethyl Acetoacetate and its Analogues. EMIL KNOEVENAGEL and FRITZ SCHRÖDER (*Ber.*, 1904, **37**, 4484—4491. Compare Gattermann and Horlacher, Abstr., 1899, i, 372).—*Acetylnaphthacoumarin*,

$$\begin{array}{l}CH{:}CH\cdot C\cdot CH{:}CH\cdot C\cdot O\text{—}CO\\ |\qquad\quad\;\; \|\qquad\qquad\;\; \|\quad\; |\\ CH{:}CH\cdot C\text{————}C\cdot CH{:}CAc\end{array},$$

obtained by warming β-hydroxy α-naphthaldehyde and ethyl acetoacetate with piperidine in alcoholic solution, crystallises in leaflets, melts at 186°, and dissolves in concentrated sulphuric acid to a blood-red, or in 10 per cent. aqueous potassium hydroxide to a brownish-red

solution. The *phenylhydrazone*, $C_{21}H_{16}O_2N_2$, crystallises in matted, scarlet needles and melts at 209°. *Benzoylnaphthacoumarin*,

$$C_{10}H_6<\begin{matrix}O\text{---}CO \\ CH:CBz\end{matrix},$$

obtained from β-hydroxy-α-naphthaldehyde and ethyl benzoylacetate, crystallises in yellow needles and melts at 208°.

Ethyl naphthacoumarincarboxylate, $C_{10}H_6<\begin{matrix}O\text{---}CO \\ CH:C\cdot CO_2Et\end{matrix}$, obtained from β-hydroxy-α-naphthaldehyde and ethyl malonate, crystallises in matted, white needles, melts at 115°, and forms blue, fluorescent solutions. Hydrolysis of the ester leads to the formation of the *carboxylic acid*, $C_{14}H_8O_4$, which is also formed by the action of malonic acid on β-hydroxy-α-naphthylideneaniline. It melts at 231° and gives an intense yellow coloration with concentrated sulphuric acid.

β-Hydroxy-α-naphthylideneacetylacetone, $OH\cdot C_{10}H_6\cdot CH:C(COMe)_2$, crystallises in yellow needles and melts at 137°. When shaken with glacial acetic acid, it yields a yellow, flocculent *substance*, which melts and decomposes at 200—210°.

The action of ethyl cyanoacetate on β-hydroxy-α-naphthaldehyde in presence of piperidine in alcoholic solution leads to the formation of *ethyl cyanonaphthacoumarincyanoacetate*, $C_{19}H_{14}O_4N_2$, which crystallises in yellow needles, melts and decomposes at 283°, and is decomposed by boiling glacial acetic acid to a yellow nitrogenous *substance* melting at 112°. G. Y.

Condensation of Salicylaldehyde and of β-Hydroxy-α-naphthaldehyde with Ethyl Acetonedicarboxylate. EMIL KNOEVENAGEL and E. LANGENSIEPEN (*Ber.*, 1904, **37**, 4492—4496).—Salicylaldehyde (1 mol.) and ethyl acetonedicarboxylate (1 mol.) condense in presence of piperidine to form *ethyl coumarinketoacetate*, $C_6H_4<\begin{matrix}O\text{—}CO \\ CH:C\cdot CO\cdot CH_2\cdot CO_2Et\end{matrix}$, which crystallises in slender, white needles, melts at 104°, and, on hydrolysis, yields the *acid*, $C_{10}H_6O_4$; this crystallises in colourless needles and melts at 187°.

Dicoumarin ketone, $C_{19}H_{10}O_5$, is formed by condensation of ethyl coumarinketoacetate with salicylaldehyde, or of ethyl acetonedicarboxylate (1 mol.) with salicylaldehyde (2 mols.). It forms small, white crystals and melts at 234°. The *oxime*, $C_{19}H_{11}O_5N$, crystallises in long, glistening needles and melts at 251°. When warmed with aqueous potassium hydroxide or sodium carbonate, dicoumarin ketone dissolves to a red solution, addition of hydrochloric acid to which precipitates *coumarinketocoumaric acid*,

$$C_6H_4<\begin{matrix}O\text{---}CO \\ CH:C\cdot CO\cdot C(CO_2H):CH\cdot C_6H_4\cdot OH\end{matrix};$$

the acid crystallises in small, white needles, melts at 259—260°, and yields dicoumarin ketone when treated with acetic anhydride.

Ethyl naphthacoumarinketoacetate, $C_{10}H_6<\begin{matrix}O\cdot CO \\ CH:C\cdot CO\cdot CH_2\cdot CO_2Et\end{matrix}$, forms a yellow, crystalline mass, melts at 151—152°, and, on hydrolysis,

yields naphthacoumarincarboxylic acid, $C_{14}H_{14}O_4$, which melts at 232° (see foregoing abstract). G. Y.

Condensation of Salicylaldehyde with Ethyl Cyanoacetate, Ethyl Benzoylacetate, or Acetylacetone. Emil Knoevenagel and Robert Arnot (*Ber.*, 1904, **37**, 4496—4502. Compare Abstr., 1898, i, 406; 1899, i, 116).—Salicylaldehyde reacts with ethyl cyanoacetate, in presence of piperidine, to form ethyl salicylidenebiscyanoacetate (Beccari, Abstr., 1902, i, 371), which melts at 139—140°, yields ammonia and salicylaldehyde when boiled with dilute alkali hydroxides, and when boiled with water is decomposed to a white substance, which melts at 85°, and a product which melts and decomposes at 180—250°. *β-2-Hydroxyphenylpropane-ααγ-tricarboxylic anhydride*,

$$\begin{array}{l} CH{:}CH{\cdot}C{\cdot}O{\cdot}CO{\cdot}CH{\cdot}CO{-}O \\ | \qquad\quad\ \ \| \qquad\qquad\quad | \qquad\qquad | \\ CH{:}CH{\cdot}C{-\!-\!-\!-\!-}CH{\cdot}CH_2{\cdot}CO \end{array}$$

formed when ethyl salicylidenebiscyanoacetate is boiled with dilute hydrochloric acid, crystallises in white leaflets and melts at 85—86°.

Benzoylcoumarin, $C_{16}H_{10}O_3$, obtained by the condensation of salicylaldehyde and ethyl benzoylacetate in presence of piperidine, crystallises in white needles and melts at 130°.

Salicylidenebispiperidine, $C_{17}H_{26}ON_2$, formed by the condensation of salicylaldehyde with piperidine, melts at 86—87° and, when warmed with ethyl benzoylacetate, yields benzoylcoumarin. The *oxime*, $C_{16}H_{11}O_3N$, of the latter crystallises in white needles and melts at 148—150°.

Salicylideneacetylacetone, $C_{12}H_{12}O_3$, obtained by condensation of salicylaldehyde with acetylacetone, forms white crystals, melts at 85°, and forms a yellow *additive* compound with bromine, and a *potassium* salt which crystallises in glistening, green needles. The *oxime*, $C_{12}H_{13}O_3N$, crystallises in white leaflets and melts at 110°. Addition of dilute acids to the alcoholic solution of salicylideneacetylacetone results in the formation of a white, crystalline *compound*, $C_{15}H_{16}O_3$, which melts and decomposes at 105° and, on recrystallisation from hot water, forms yellow needles which melt at 109°. The action of dilute acids on the substance melting at 105°, or prolonged boiling of the substance melting at 109° with water, leads to the formation of a *compound* which melts and decomposes at 70—75°. The action of dilute nitric acid at 130° under pressure on the substance melting at 105°, leads to the formation of a yellow nitrogenous *substance* which melts at 113° and forms an explosive *potassium* salt crystallising in yellow needles. The *oxime*, $C_{15}H_{16}O_2{:}NOH$, melts at 118°; the *phenylhydrazone* melted, when impure, at 125—130°.

G. Y.

Condensation of Aliphatic Nitro-compounds with Aromatic Aldehydes by means of Organic Bases. Emil Knoevenagel and Leonhard Walter (*Ber.*, 1904, **37**, 4502—4510).—Aromatic aldehydes (benzaldehyde, piperonal, anisaldehyde, vanillin) form condensation products with primary aliphatic nitro-compounds (nitromethane, nitroethane, phenylnitromethane) in presence of amylamine, ethyl-

amine, or methylamine carbonate, less rapidly in presence of piperidine or diethylamine. The following new compounds are described :

Anisylidenenitromethane, $C_9H_9O_3N$, crystallises in slender, yellow needles or plates and melts at 86°. *Vanillylidenenitromethane*, $C_9H_9O_4N$, melts at 165°.

Piperonylidenenitroethane, $C_{10}H_9O_4N$, crystallises in golden needles and melts at 98°. *Anisylidenenitroethane*, $C_{10}H_{11}O_3N$, forms long, yellow, prismatic crystals and melts at 48°.

Phenylbenzylidenenitromethane, $C_{14}H_{11}O_2N$, crystallises in yellow leaflets and melts at 75°.

Phenylpiperonylidenenitromethane, $C_{15}H_{11}O_4N$, forms yellow crystals and melts at 124°.

Phenylanisylidenenitromethane, $C_{15}H_{13}O_3N$, crystallises in broad, golden needles and melts at 151°. G. Y.

Oxidising Chlorination of *o*-Hydroxybenzaldehyde and of *p*-Hydroxybenzaldehyde. HEINRICH BILTZ (*Ber.*, 1904, **37**, 4448).—An analytical correction (compare Abstr., 1904, i, 1021).

W. A. D.

The Occurrence of Vanillin. EDMUND O. VON LIPPMANN (*Ber.*, 1904, **37**, 4521—4522).—The odour of vanillin is frequently noticeable in the neighbourhood of saw-mills. A shaving of wood taken in one case when the odour was exceptionally strong yielded sufficient vanillin on extraction with ether to allow of recrystallisation and identification. Vanillin has been previously recognised in wood (compare Seidel, *Zeit. angew. Chem.*, 1898, 876 ; Bräutigam, Abstr., 1901, i, 93 ; Grafe, this vol., i, 23). C. H. D.

Hydrogenation of Aromatic Ketones by means of Reduced Nickel. New Method of Synthesising Aromatic Hydrocarbons. GEORGES DARZENS (*Compt. rend.*, 1904, **139**, 868—870).—When aromatic ketones of the type COPhR are directly hydrogenated at 190—195° in the presence of nickel obtained by reducing nickel oxide at 300°, the reaction proceeds according to the following equation : $COPhR + 2H_2 = CH_2PhR + H_2O$; if, however, the nickel employed has been obtained by reducing the oxide at a temperature below 300°, it behaves as a more active catalyst (compare Sabatier and Senderens, Abstr., 1903, i, 733), and the corresponding hexahydro-derivative of the benzene homologue is obtained. The following homologues of benzene were prepared : ethylbenzene, boiling at 136—137°, from acetophenone ; *p*-methylethylbenzene, boiling at 158—162°, from *p*-tolyl methyl ketone ; p-*ethyl*-tert.-*butylbenzene*, from *p*-butylacetophenone, boils at 209—213° and has an odour similar to that of carrots ; and butylbenzene, boiling at 180°, from benzylacetone. M. A. W.

Beckmann's Rearrangement by means of Benzene Sulphonic Chloride in the Presence of Alkali or Pyridine. ALFRED WERNER and A. PIGUET (*Ber.*, 1904, **37**, 4295—4315).—The Beckmann reaction under the influence of benzenesulphonic chloride proceeds well in pyridine solution, and the isolation of the primary products is more readily effected than when an alkaline solution is used.

In the case of α- or *o*-diketonemonoximes, the rearrangement may

take place in two ways; the hydroxyl at first attached to nitrogen becoming attached either to the carbon atom immediately linked with the nitrogen, or to the carbon atom connected with the ketonic oxygen. The second form of the reaction occurs especially with the oximes of cyclic *o*-diketones.

γ-Benzilmono-oxime is converted by benzenesulphonic chloride in sodium hydroxide or pyridine solution into the *compound*

$$\begin{array}{l} SO_2Ph\cdot O\cdot C\cdot COPh \\ \qquad\quad\;\; \| \\ \qquad\;\; Ph\cdot N \end{array},$$

which crystallises from alcohol in colourless, prismatic needles melting at 114°, and may be regarded as the benzenesulphonic ester of the product of the Beckmann rearrangement, $\begin{array}{l} OH\cdot C\cdot COPh \\ \quad\;\; \| \\ Ph\cdot N \end{array}$. Alcoholic potassium hydroxide converts it into phenylcarbylamine and benzoic and benzenesulphonic acids; dilute sulphuric acid forms aniline, benzonitrile, and benzenesulphonic acid. An attempt to synthesise the compound from benzoylformanilide and benzenesulphonic chloride was unsuccessful.

Under the same conditions, α-benziloxime yields the *compound* $\begin{array}{l} Ph\cdot C\cdot O\cdot COPh \\ \quad\;\; \| \\ \quad\;\; N\cdot COPh \end{array}$, crystallising from acetic acid in large, colourless prisms melting at 95°, and yielding ammonia and benzonitrile or benzoic acid on hydrolysis. It is therefore the benzoyl ester of the normal product, benzoic acid being produced by a rearrangement of the second type. The stereochemical formulæ proposed for the benziloximes by Beckmann and Köster (Abstr., 1893, i, 474) are thus confirmed (compare Hantzsch and Werner, Abstr., 1890, 970).

Both the α- and β-oximes of benzoylformic acid yield only benzonitrile; deoxybenzoinoxime yields phenylacetanilide, $NHPh\cdot CO\cdot CH_2Ph$, crystallising in colourless prisms and melting at 117°. Benzophenoneoxime yields only benzanilide.

Both *anti*- and *syn*-benzaldoximes yield benzonitrile. Camphoroxime yields campholenonitrile.

α-Benzoinoxime yields benzonitrile and benzaldehyde (rearrangement of the second type). β-Benzoinoxime behaves normally, yielding phenylglycollanilide, $NHPh\cdot CO\cdot CHPh\cdot OH$. The formulæ to be assigned to the oximes are therefore: α-oxime, $\begin{array}{l} Ph\cdot C\cdot CHPh\cdot OH \\ \quad\;\; \| \\ \quad\;\; N\cdot OH \end{array}$; β-oxime,

$$\begin{array}{l} Ph\cdot C\cdot CHPh\cdot OH \\ \quad\;\; \| \\ OH\cdot N \end{array}.$$

α-Nitroso-β-naphthol reacts with either benzenesulphonic chloride or sulphuryl chloride in pyridine solution to form *o*-cyanocinnamic acid, a reaction of the second type. In similar manner, phenanthraquinoneoxime yields *2-cyanodiphenyl-2'-carboxylic acid*, $CN\cdot C_6H_4\cdot C_6H_4\cdot CO_2H$, crystallising from benzene in colourless prisms and melting at 170—172°; the *methyl* ester forms long double-pyramids and melts at 79—80°. 2-Nitrophenanthraquinoneoxime yields a *nitro-2-cyanodiphenyl-2'-carboxylic acid*, crystallising in pale yellow prisms melting at 194—195°; the *methyl* ester forms colourless needles and melts at 123—124°. 2 : 7-Dinitrophenanthraquinoneoxime yields a *dinitro-2-cyanodiphenyl-*

2'-carboxylic acid, crystallising in colourless leaflets melting at 217—218°; the *methyl* ester forms small prisms melting at 149—150°. Retenequinoneoxime yields the *mononitrile* of *methyl*iso*propyldiphenic acid,* $C_{18}H_{17}O_2N$, forming small, colourless crystals melting at 195°.

Acenaphthaquinoneoxime yields the *imide* of *naphthalic acid,* $C_{12}H_7O_2N$, crystallising in small, colourless needles and melting at 290—291°. The solution in concentrated sulphuric acid shows an intense blue fluorescence. C. H. D.

Condensation of Diphenic Anhydride with Toluene. Hans Pick (*Monatsh.*, 1904, **25**, 979—986. Compare Götz, Abstr., 1902, i, 372).—Fluorenone-5-carboxylic acid and *p*-toluoyl-5-fluorenone are formed when diphenic anhydride in toluene solution is warmed with aluminium chloride.

4-p-*Toluoylfluorenone*, $\begin{matrix} CO\text{—}C{:}CH\text{———}CH \\ | \quad\quad | \quad\quad\quad\quad\quad\quad || \\ C_6H_4\cdot C{:}C(CO\cdot C_7H_7)\cdot CH \end{matrix}$, is better formed by the action of aluminium chloride on fluorenone-5-carboxylic chloride in toluene solution; it crystallises in yellow, prismatic needles, melts at 128°, dissolves in concentrated sulphuric acid to an orange-red solution, and forms a *phenylhydrazone*, $C_{27}H_{20}ON_2$, which decomposes at 82°. 4-p-*Methylbenzylfluorene*, $\begin{matrix} CH_2\text{—}C{:}CH\text{———}CH \\ | \quad\quad | \quad\quad\quad\quad\quad\quad || \\ C_6H_4\cdot C{:}C(CH_2\cdot C_7H_7)\cdot CH \end{matrix}$, obtained by heating toluoyl-5-fluorenone with zinc dust, crystallises in white needles and melts at 72°.

The condensation of fluorenone-4-carboxylic chloride with anisole in presence of aluminium chloride leads to the formation of 4-p-*methoxybenzoylfluorenone*, $\begin{matrix} CO\text{—}C{:}CH\text{————}CH \\ | \quad\quad | \quad\quad\quad\quad\quad\quad\quad || \\ C_6H_4\cdot C{:}C(CO\cdot C_6H_4\cdot OMe)\cdot CH \end{matrix}$, which forms white crystals and melts at 95°. G. Y.

Condensations of *o*-Aldehydocarboxylic Acids with Ketones. Alfred Luksch (*Monatsh.*, 1904, **25**, 1051—1064. Compare Zink, Abstr., 1902, i, 34).—*Meconinemethyl ethyl ketone*,

$$\begin{matrix} OMe\cdot C{:}C(OMe)\cdot C\cdot CO\cdot O \\ | \quad\quad\quad\quad || \quad\quad | \\ CH{=}CH\text{—}C\text{——}CH\cdot CH_2\cdot COEt \end{matrix},$$

formed by the action of opianic acid on methyl ethyl ketone in aqueous sodium hydroxide solution at 35°, crystallises in white needles, melts at 128—132°, is soluble in hot water or alcohol, dissolves in boiling aqueous alkali carbonates, and is decomposed by hot aqueous potassium hydroxide. The *oxime* forms small, glistening crystals and melts at 109—112°.

Meconinemethyl propyl ketone, $C_{10}H_9O_4\cdot CH_2\cdot COPr^{\alpha}$, crystallises in small needles, melts at 91—95°, is soluble in warm water, alcohol, ether, benzene, chloroform, or glacial acetic acid, and is decomposed by warm aqueous potassium hydroxide. The *oxime* melts at 153—157°. *Meconinemethyl* iso*propyl ketone*, $C_{10}H_9O_4\cdot CH_2\cdot COPr^{\beta}$, melts at 88—91° and is soluble in hot water or alcohol. With hydroxylamine hydrochloride in alcoholic solution, or with hydroxylamine in alcoholic sodium hydroxide solution, it forms the *oxime* of the "pseudo-acid" (compare Fulda, Abstr., 1900, i, 36), $C_{15}H_{19}O_5N$, which crystallises in matted, white

needles, melts at 110°, and is soluble in warm water, alcohol, or benzene or in cold acetone, chloroform, or glacial acetic acid; it has a neutral action towards litmus and dissolves in aqueous alkali hydroxides or carbonates only on warming. When heated to its melting point, it undergoes isomeric change into the *oxime* of the acid, which is also formed by the action of hydroxylamine on the ketone at 100° in alcoholic solution; this oxime crystallises in colourless, glistening, silky needles, melts at 223°, is less soluble in warm water or alcohol than its isomeride, dissolves readily in cold aqueous alkali hydroxides, slowly in cold aqueous alkali carbonates, and can be titrated directly.

The action of aqueous ammonia on meconinemethyl ethyl and meconinemethyl propyl ketones, leads to the formation of yellow, transparent resins.

Meconinemethyl *iso*propyl ketone and concentrated aqueous ammonia form the *hydroxy-amide*,

$$NH_2\cdot CO\cdot C_6H_2(OMe)_2\cdot CH(OH)\cdot CH_2\cdot COPr^{\beta},$$

which separates in white crystals, melts at 141—143°, and is easily soluble in hot water or alcohol. It dissolves in concentrated sulphuric acid to a carmine solution, which, when heated, becomes green and finally violet, and yields a brown, flocculent precipitate on addition of water; when boiled with dilute acids, it is hydrolysed with formation of ammonia. When boiled with glacial acetic acid, it yields the *acetyl* derivative, $C_{17}H_{23}O_6N$, which crystallises in glistening, white leaflets, melts at 187°, and, when treated with sodium nitrite in acetic acid solution, forms meconinemethyl *iso*propyl ketone. G. Y.

Quinone Imines. III. RICHARD WILLSTÄTTER and ADOLF PFANNENSTIEL (*Ber.*, 1904, **37**, 4605—4609. Compare Willstätter and Mayer, Abstr., 1904, i, 511).—Quinonedi-imine, $C_6H_6N_2$, prepared by the oxidation of an ethereal solution of *p*-phenylenediamine by dry silver oxide, separates in colourless needles, which gradually assume a grey to brownish-yellow tint. It forms colourless solutions; it explodes on the addition of concentrated hydrochloric or sulphuric acids, but by careful treatment with pure sulphuric acid its sulphate may be isolated. When quickly heated, it becomes coloured at 75° and melts at about 124°.

Quinonemonoimine, prepared by the oxidation of an ethereal solution of *p*-aminophenol by dry silver oxide, separates in prisms or needles, which although momentarily colourless, gradually assume a yellowish-grey to brown colour on being exposed to air. It is more unstable than the di-imine and decomposes spontaneously when separated from its ethereal solution, red fumes being evolved. When warmed with dilute sulphuric acid, it is converted into quinone and ammonia; by stannous chloride and hydrochloric acid, it is reduced to *p*-aminophenol. It is more soluble in ether than is the di-imine. With phenol and alkali, it forms a deep blue solution, which, when acidified, turns red, and forms a bluish-green layer when concentrated sulphuric acid is carefully added.

By comparison of those imines with quinone and with Thiele's fulvenes, it appears that, contrary to the current views, the group C:NH is a weaker chromophore than the group C:O or C:C. A. McK.

Nitroamines of the Anthraquinone Series. ROLAND SCHOLL [and, in part, G. SCHNEIDER and F. EBERLE] (*Ber.*, 1904, **37**, 4427—4448).—The nitration of the aminoanthraquinones is remarkable as giving rise to nitroamines as direct products.

On gradually adding at $-10°$ finely powdered 2-aminoanthraquinone to nitric acid of sp. gr. 1·50 which has been freed from nitrous acid by means of carbamide, a mixture of *3-nitro-2-nitroaminoanthraquinone*, $C_6H_4:(CO)_2:C_6H_2(NO_2)\cdot NH\cdot NO_2$, and 1 : *3-dinitro-2-nitroaminoanthraquinone* is obtained, which can be resolved into its constituents by recrystallisation from acetone. *3-Nitro-2-nitroaminoanthraquinone* separates, on adding water, in yellow crystals, and when pure explodes at a temperature intermediate between 180° and 191°, depending on the rate of heating; when heated with phenol and sulphuric acid, it shows Liebermann's reaction in a modified manner, a brownish-purple solution being produced which changes to green; the *sodium* salt, $C_6H_4:(CO)_2:C_6H_2(NO_2)\cdot N<\genfrac{}{}{0pt}{}{O}{N\cdot ONa}$, of the nitroamine forms orange-red crystals and decomposes at 245°. On agitating the nitroamino-compound with a mixture of phenol (1 part) and concentrated sulphuric acid (10 parts), it is converted into *3-nitro-2-aminoanthraquinone*, which crystallises from xylene and melts at 305—306°; the structure of this follows from its conversion by the diazo-reaction into 2-nitroanthraquinone, which melts at 184·5—185° (corr.) (compare Kaufler, Abstr., 1904, i, 256) and is reducible by ammonium sulphide to 2-aminoanthraquinone.

3-Nitro-1-hydroxyanthraquinone, obtained by passing gaseous nitrous acid into a solution of 3-nitro-2-nitroaminoanthraquinone in fuming nitric acid and boiling the product with alcohol, crystallises from glacial acetic acid in yellow leaflets and melts at 247—248°; its structure was not established, but appears probable in view of the action of fuming nitric acid on 2-aminoanthraquinone (*infra*); *3-amino-1-hydroxyanthraquinone* forms slender, red needles and sublimes without melting.

1 : *3-Dinitro-2-nitroaminoanthraquinone* is more soluble in acetone than its congener, separates from ether in bright yellow crystals, and decomposes at 99°; when agitated with phenol and sulphuric acid, it gives 1 : *3-dinitro-2-aminoanthraquinone*, which crystallises from glacial acetic acid in yellow prisms, melts at 279—280°, and is reduced by ammonium sulphide to 1 : 2 : *3-triaminoanthraquinone*, which crystallises from nitrobenzene and does not melt at 300°.

3-Nitro-2-nitroamino-1-hydroxyanthraquinone is formed together with 1 : 3-dinitro-2-nitroaminoanthraquinone when 2-aminoanthraquinone is nitrated with nitric acid of sp. gr. 1·52 at 35—40°; it crystallises from glacial acetic acid in yellowish-red needles and decomposes at 234°.

2 : *6-Dibromo-4* : *8-dinitro-1* : *5-dinitrodiaminoanthraquinone*,

$$C_{14}H_2O_2Br_2(NO_2)_2(NH\cdot NO_2)_2,$$

prepared by adding finely powdered 2 : 6-dibromo-1 : 5-diaminoanthraquinone to colourless nitric acid of sp. gr. 1·52, forms a microcrystalline powder and decomposes at 142—143°; it is nearly insoluble in all solvents; the crystalline *disodium* salt, $C_{14}H_2O_{10}N_6Br_2Na_2$, and

the analogous *dipotassium* and *diammonium* salts are anhydrous. 2 : 6-*Dibromo*-4 : 8-*dinitro*-1 : 5-*diaminoanthraquinone*, obtained by denitrating the nitroamino-derivative with phenol and sulphuric acid at the ordinary temperature, separates from phenol or nitrobenzene, in which it is very sparingly soluble, in red crystals having a metallic lustre, and does not melt up to 360°.

2 : 4 : 6 : 8-*Tetrabromo*-1 : 5-*dinitrodiaminoanthraquinone*, prepared by nitrating tetrabromo-1 : 5-diaminoanthraquinone, forms a bright yellow, crystalline powder and explodes at 166°; it is denitrated by simply heating it with alcoholic hydrochloric acid, giving 2 : 4 : 6 : 8-*tetrabromo*-1 : 5-*diaminoanthraquinone*.

2 : 4 : 6 : 8-*Tetranitro*-1 : 5-*dinitrodiaminoanthraquinone*, obtained by nitrating 1 : 5-diaminoanthraquinone with ice-cold nitric acid of sp. gr. 1·52, forms a yellow, crystalline powder and explodes when gently heated or when struck; 2 : 4 : 6 : 8-*tetranitro*-1 : 5-*diaminoanthraquinone* is a dark coloured powder. W. A. D.

Xanthogen Reaction and its Application to the Terpene and Camphor Series. II. L. A. Tschugaeff (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 988—1052. Compare Abstr., 1904, i, 327).—In the transformation of an alcohol of the terpene or camphor series into a hydrocarbon, isomeric change often takes place. In order to avoid this change, the author applies to such cases the xanthogen reaction, by which means he is able to obtain the hydrocarbon directly corresponding with the alcohol employed.

The first case to which this procedure is applied is that of dihydrocarveol, which is formed by the reduction of *d*-carvone by means of sodium in alcoholic solution. The dihydrocarveol is first converted into sodium dihydrocarvylxanthate, $C_{10}H_7O{\cdot}CS_2Na$, by acting on its toluene solution with ether and carbon disulphide. The sodium salt is then transformed into the corresponding methyl dihydrocarvylxanthate, which, on dry distillation, decomposes thus: $C_{10}H_{17}O{\cdot}CS_2Me = C_{10}H_{16} + CSO + CH_3{\cdot}SH$. The hydrocarbon thus obtained is a mixture of the two compounds: (1) *l*-limonene and (2) an isomeric substance, to which the author assigns the name iso*limonene* and the structure $CHMe{<}{\substack{CH{=}CH\\ CH_2{\cdot}CH_2}}{>}CH{\cdot}CMe{:}CH_2$. It boils at 172—173° under 754 mm. pressure, has the sp. gr. 0·8374 at 20°/4°, n_D 1·46997, and $[\alpha]_D - 140{\cdot}11°$. No tetrabromide or nitrosochloride could be obtained. On long boiling in presence of potassium, *iso*limonene undergoes isomeric change into a terpene. With hydrogen bromide, *iso*limonene yields dipentene dihydrobromide melting at 63—64°. All the properties of *iso*limonene indicate that its relation to limonene is similar to that which carvomenthene bears to Δ^2-menthene.

It is found that dihydrocarveol, obtained by the reduction of *d*-carvone, consists of a mixture of two isomerides, since, under the action of alcoholic ammonia solution, methyl dihydrocarvylxanthate yields two amides: (1) *a-dihydrocarvylxanthamide*, $C_{11}H_{19}ONS$, which separates from light petroleum in colourless crystals melting at 62·5—63·5°; it is extremely readily soluble in ether, alcohol, chloroform, or benzene, and, to a less extent, in light petroleum; has

$[\alpha]_D + 135\cdot33°$ ($c = 9\cdot226$) or $139\cdot03$ ($c = 2\cdot916$), and its molecular weight in freezing benzene has the normal value. When treated with excess of concentrated alcoholic potassium hydroxide solution, the α-amide is converted into *α-dihydrocarveol*, which boils at 222·5—222·8° under 749 mm. pressure, and has the sp. gr. 0·9204 at 20°/4°, n_D 1·47818 at 20°, and $[\alpha]_D + 33\cdot86°$. (2) An isomeric amide, which was not obtained pure.

A new method for hydrolysing xanthamides consists in treating them with one of Grignard's organo-magnesium compounds, which acts on the tautomeric (sulphydryl) form of amide, thus: $RO\cdot C(SH)\colon NH + MeMgI = RO\cdot C(SMgI)\colon NH + CH_4$; the compound thus obtained is then decomposed by excess of water yielding ROH.

The above method is also applied to thujone. The author is of opinion that the thujene obtained by Wallach and the tanacetene of Semmler correspond, not with thujone, but with a product of its isomerisation, *iso*thujone. Starting from thujyl alcohol, he has prepared, by the processes described, *methyl thujylxanthate*,

$$C_{10}H_{17}O\cdot CS_2Me,$$

which has the sp. gr. 1·0569 at 20°/4°, $[\alpha]_D + 63\cdot87°$, and n_D 1·53572 at 20°. On dry distillation of this methyl ester, part of it undergoes ready decomposition, yielding a hydrocarbon to which the author gives the name *α-thujene* and the constitution $CH_2{<}\begin{matrix} CH\text{—}CMe \\ | \\ CPr^{\beta}\cdot CH_2 \end{matrix}{>}CH$; α-thujene is a colourless, mobile liquid, which boils at 152—152·5° under 748 mm. pressure, has the sp. gr. 0·8275 at 20°/4°, n_D 1·45042, and $[\alpha]_D - 4\cdot23°$. It gives no crystalline nitrosochloride, but reacts readily with bromine, hydrogen bromide being evolved. With hydrogen bromide, it yields a dihydrobromide, $C_{10}H_{16},2HBr$, melting at 58—59°. From its melting point and other properties, this is evidently the dihydrobromide of dipentene, a conclusion confirmed by the fact that on distillation with quinoline it yields limonene; the formation of this dihydrobromide is doubtless the result of isomeric change. α-Thujene is comparatively stable towards the action of heat, and only at 300—310° does it show signs of undergoing isomeric change, yielding a compound which is probably *iso*thujene.

The portion of the methyl thujylxanthate which does not readily decompose was subjected to a higher temperature, the product of the distillation being *β-thujene*, $CH_2{<}\begin{matrix} CH\cdot CHMe \\ | \\ CPr^{\beta}\text{—}CH \end{matrix}{>}CH$, which boils at 150—151° under 750 mm. pressure and has $[\alpha]_D + 77\cdot43°$, the sp. gr. 0·8248 at 20°/4° and 0·8232 at 22°/4°, and n_D 1·44842 at 22°.

That α-thujene is the hydrocarbon corresponding with thujone is confirmed by preparing it from the latter by way of the oxime and amine. Thujoneoxime separates from ether in crystals melting at 53°, is readily soluble in all organic solvents, and has $[\alpha]_D + 107\cdot46°$. On boiling with sodium in alcoholic solution, it is reduced to thujylamine, the *hydrochloride* of which, $C_{10}H_{17}\cdot NH_2,HCl$, melts at 260°, and has $[\alpha]_D + 79\cdot36°$, whilst the nitrate forms prismatic crystals melting at 167—168° and having $[\alpha]_D + 70\cdot37°$. *Thujyltrimethylammonium iodide*, $C_{10}H_{17}NMe_3I$, separates in colourless crystals,

slightly soluble in water or alcohol, and more readily in chloroform; it has $[\alpha]_D$ $+42{\cdot}61°$. The action of silver oxide on this compound yields *thujyltrimethylammonium hydroxide*, which forms a viscid, non-crystalline mass, and, on heating, decomposes into trimethylamine and α-thujene.

Thujyldimethylamine, $C_{10}H_{17}NMe_2$, is a colourless liquid which boils at 213·5—214°, has the sp. gr. 0·8606 at 20°/4° and $[\alpha]_D$ $+148{\cdot}76°$; its *hydrochloride*, *platinichloride*, *nitrate*, and *picrate* were prepared.

On reducing *iso*thujone to thujamenthol, converting the latter into the corresponding methyl xanthic ester, $C_{10}H_{19}OCS_2Me$, and distilling this, the hydrocarbon *thujamenthene*, $C_{10}H_{18}$, is obtained as a liquid boiling at 157—159° under 750 mm. pressure, and having the sp. gr. 0·8046 at 20°/4° and n_D 1·44591. Thujamenthene is optically inactive, and yields a crystalline nitrosochloride.

Methyl bornylxanthate, $C_{10}H_{17}O{\cdot}CS_2Me$, obtained in both dextro- and lævo-modifications by the method given above, separates from alcohol in rhombic crystals [$a:b:c = 2{\cdot}0981:1:1{\cdot}4429$] melting at 56—57°, and is soluble in benzene, toluene, chloroform, or ether. The lævo-modification has $[\alpha]_D$ $-33{\cdot}38°$ ($c = 13{\cdot}004$) in benzene and $-41{\cdot}55°$ ($c = 12{\cdot}952$) in ethyl acetate, whilst for the dextro-compound the values are $+33{\cdot}69°$ in benzene and $+41{\cdot}45°$ in ethyl acetate. On hydrolysis with alcoholic potassium hydroxide solution, these esters give respectively *l*- and *d*-borneols with $[\alpha]_D$ $-38{\cdot}23°$ and $+38{\cdot}39°$. The racemic ester melts at 28·5—29°, but does not readily crystallise; it has the sp. gr. 1·0923 at 20°/4° and 1·0084 at 25·3°/4° and the n_D 1·54829 at 26°. On dry distillation, methyl bornylxanthate (from *l*-borneol) yields a new d-*terpene*, $C_{10}H_{16}$, which boils at 149° under 745 mm. pressure, melts at 103—104°, and has $[\alpha]_D$ $+13{\cdot}77°$. The corresponding lævo-*compound* has $[\alpha]_D$ $-12{\cdot}61°$.

Ethyl bornylxanthate melts at 52—53°, forms hemihedral crystals of the rhombic system [$a:b:c = 2{\cdot}0809:1:1{\cdot}4623$], and dissolves readily in the ordinary solvents. The lævo-form has $[\alpha]_D$ $-30{\cdot}54°$ in benzene and $-32{\cdot}96°$ in toluene, the value for the dextro-form being $+33{\cdot}35°$ in toluene. The racemic modification melts at 28—29° and has the sp. gr. 1·0709 at 20°/4° and n_D 1·54396.

Bornyldixanthide, $(C_{10}H_{17}O{\cdot}CS)_2S_2$, is readily obtained by the action of iodine in benzene or ethereal solution on sodium bornylxanthide: $2C_{10}H_{17}O{\cdot}CS_2Na + I_2 = (C_{10}H_{17}O{\cdot}CS)_2S_2 + 2NaI$. Both dextro- and lævo-forms melt at 82—83° and crystallise from alcohol in long, yellowish-white needles, or, on slow evaporation of a solution in a mixture of alcohol and ether, in long prisms readily forming twin crystals. The dextro-form has $[\alpha]_D$ $+43{\cdot}79°$ and the lævo-form $-44{\cdot}12°$ in benzene. The racemic modification crystallises from ether in yellow needles melting at 81—82°.

Bornylxanthamide, $C_{10}H_{17}O{\cdot}CS{\cdot}NH_2$, is readily prepared by the action of alcoholic ammonia solution on methyl bornylxanthate. Both the optical antipodes melt at 125—126° and separate from a mixture of light petroleum in drusy masses of prismatic crystals. Both exhibit distinct triboluminescence, and dissolve readily in alcohol, ether, benzene, or chloroform. The *d*-amide has $[\alpha]_D$ $+18{\cdot}95°$

and the *l*-amide $-18{\cdot}13°$ in benzene. The racemic form separates in needles or prisms melting at 134·5—135·5°.

ab-*Diphenyl-c-bornyliminoxanthide*, $C_{10}H_{17}O{\cdot}CS{\cdot}S{\cdot}CPh{:}NPh$ or $C_{10}H_{17}O{\cdot}CS{\cdot}NPh{\cdot}CSPh$, is prepared by the interaction of sodium bornylxanthate and chlorodiphenylimide, CPhCl:NPh. Both *d*- and *l*-forms melt at 87—88° and the racemic modification at 89—90°.

T. H. P.

Crystalline Products of the Ethereal Oil of the Siberian Fir. P. Golubeff (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 1096—1108).—The following two compounds have been separated by the author from the ethereal oil of the Siberian Fir (*Abies sibirica*).

(1) *Borneol acetate*, $C_{10}H_{17}{\cdot}OAc$, which crystallises in the rhombic system [$a:b:c = 1{\cdot}44:1:0{\cdot}67$], melts at 29° and boils at 223—224° under 758·3 mm. pressure; it dissolves readily in alcohol, ether, or acetic acid, and to a still greater extent in light petroleum; its heat of combustion is 8540 cals. per 1 gram and it has $[\alpha]_D$ $-45{\cdot}47°$ at 20°. On hydrolysis, it yields a *borneol*, $C_{10}H_{18}O$, which crystallises from light petroleum in thin, hexagonal plates, melts at 204°, and boils at 210° under 778·8 mm. pressure; it has an aromatic odour and is soluble in the same liquids as its acetate, although to a less degree; its heat of combustion is 95·44 cals. and it has $[\alpha]_D$ $-36{\cdot}14°$ in alcohol. On oxidation, it yields a l-*camphor*, $C_{10}H_{16}O$, which melts at 188—189°, boils at 204° under 756·6 mm. pressure, and has $[\alpha]_D$ $-41{\cdot}11°$ in alcoholic solution; its heat of combustion is the same as that of ordinary Japanese camphor, namely, 9335 cals.

(2) *Camphene*, $C_{10}H_{16}$, which solidifies in needles arranged in feathery masses melting at 40—41° and boiling at 159—160°; its heat of combustion is 10,831 cals. and it has $[\alpha]_D$ $-85°$. T. H. P.

Quercitrin D. H. Brauns (*Arch. Pharm.*, 1904, **242**, 561—562).—When dried in the air, quercitrin has the composition $C_{21}H_{20}O_{11},2H_2O$. It loses its water completely at 130°, or at 100° under diminished pressure. When the dried substance was exposed to the air, less of this water was taken up again, according as the temperature at which the substance had been dried was higher. C. F. B.

The So-called Scammonose. Emil Votoček and R. Vondráček (*Ber.*, 1904, **37**, 4615—4616).—Scammonin, obtained from the bulbs of *Convolvulus scammonia*, was converted by baryta into scammonic acid, which yielded a mixture of sugars in which methylpentoses were present. Addition of phenylmethylhydrazine caused the precipitation of rhodeosephenylmethylhydrazone. Glucosephenylosazone was also isolated. *iso*Rhodeose was probably also present.

A. McK.

Theory of Dyeing. P. D. Zacharias (*Ber.*, 1904, **37**, 4387—4388. Compare Abstr., 1902, i, 635, 725; 1903, i, 193).—Polemical. A criticism of Biltz's publications (Abstr., 1904, ii, 324, 392) on the mutual

influence of dissolved colloids and the theory of colour; it includes a claim for priority. E. F. A.

Theory of Dyes. JULES SCHMIDLIN (*Compt. rend.*, 1904, **139**, 871—873. Compare Abstr., 1904, i, 698, 785, 943, 944, 1061; this vol., ii, 11, 12).—According to the author's explanation of the difference in structure between the coloured and colourless salts of rosaniline, the amino-groups constitute the auxochromes which, uniting to form a triazine ring, cause the formation of an endothermic group containing ethylenic linkings (the chromophore) at another point of the molecule. The existence in the molecule of two groups possessing such different energies constitutes the cause of colour (compare Helmholtz, *Ann. Physik*, 1875, **154**, 582). M. A. W.

Silk and Wool as Dye Producers. HERMANN PAULY and ARTHUR BINZ (*Zeit. Farb. Text.-Ind.*, 1904, **3**, 373—374).—The authors consider that the tyrosine which is present in human nails and hair, and in silk and wool, is the cause of the dyeing of these substances when they are immersed in solutions of diazonium salts; the tyrosine, $OH\cdot C_6H_5\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$, as a phenol, gives rise to a hydroxy-azo-compound. Histidine may behave in a similar way in the case of other physiological substances which interact with diazo-salts. When *p*-phenylenedimethyldiamine is oxidised by bromine water in presence of wool or silk, a dark grey dye is produced on the fibre; a dye of the same shade is formed by a similar oxidation of the same base in presence of tyrosine, this fact probably showing that the latter substance is the source of the dye on the fibre, and that the latter is analogous to the dyes of the indophenol or oxazine series.

W. A. D.

Behaviour of Coal-tar Dyes towards Starch, Silicic Acid, and Silicates. WILHELM SUIDA (*Monatsh.*, 1904, **25**, 1107—1143).—Finely powdered potato starch was shaken with cold filtered aqueous solutions of a number of basic dyes, the liquid decanted, and the starch washed with water until the washings appeared colourless. After this treatment, the starch remained strongly coloured by the most strongly basic dyes, the colour effect decreasing with the basicity until with acid magenta, the trisulphonic acid of rosaniline, the starch, after washing with water, was almost colourless. The amount of the dye absorbed by the starch was extremely small even with the most basic dyes, 5 grams of starch taking up 0·000114 gram of magenta; the hydrochloric acid of the magenta combines with the mineral constituents of the starch. The potato starch is not coloured by dyes derived from diamines, with the exception of the azo-dyes obtained from diaminostilbene, nor by acid dyes. The behaviour of starch towards basic dyes is similar to that of animal fibres, but towards acid dyes is similar to that of cotton wool.

When shaken in the finely divided state with aqueous solutions of methylene-blue and "diamond fuchsine," sulphur, calcium, strontium, and barium sulphates, calcium, barium, magnesium, manganese, and

lead carbonates, aluminium and zinc oxides, and aluminium phosphate remained uncoloured, whilst kaolin, talc, pumice stone and kieselguhr were strongly coloured. With acid dyes, these also remained colourless. Experiments with naturally occurring silicates showed that the acid silicates were strongly coloured by magenta and methylene-blue, but that the neutral or basic silicates remained colourless or almost so. Augite and petalite form exceptions to this rule.

As a solution of phenolphthalein in water made just alkaline with ammonia and a solution of copper hydroxide in insufficient ammonia to completely dissolve it are decolorised by starch or kaolin, these substances must act as weak acids towards bases.

As in the case of starch, when kaolin is treated with a basic dye, the hydrochloric acid is quantitatively separated from the dye-base and neutralised by the mineral base; in the dyeing of wool, the acid is probably neutralised by mineral constituents or by an amine from the fibres. Kaolin is dyed red, in the same manner as is wool, when warmed with the carbinol base of triaminotriphenylmethane (Jacquemin).

By a series of experiments, it is shown that the amount of the dye (magenta, methylene-blue, crystal-violet) taken up by kaolin does not vary with the temperature or concentration of the bath, but diminishes on addition of an excess of acid.

The author concludes that the process of dyeing starch, kaolin, or wool takes place by a chemical reaction and not a physical addition.

G. Y.

Action of Methylamine and of Dimethylamine on Furfuraldehyde. FRANZ M. LITTERSCHEID (*Annalen*, 1904, **335**, 368—378. Compare Schwabbauer, Abstr., 1902, i, 230).—Furfurylidenemethylamine, formed by the action of methylamine on furfuraldehyde, without cooling, yields a *hydrochloride*, $C_4H_3O\cdot CH{:}NMe,HCl$, which crystallises in leaflets; the *platinichloride*, $(C_6H_7ON)_2,H_2PtCl_6,H_2O$, crystallises in prisms, decomposes at about 128°, and loses H_2O at 100°; the *aurichloride*, $C_6H_7ON,HAuCl_4$, forms a microscopic, crystalline precipitate and melts at about 130°; the *methiodide*, C_6H_7ON,MeI, is formed as a yellow product.

The action of methylamine on furfuraldehyde, when cooled by ice, leads to the formation of a *substance* which yields an unstable *platinichloride*, $[C_4OH_3\cdot CH(OH)\cdot NHMe]_2,H_2PtCl_6$ (?); it decomposes on drying into furfuraldehyde and methylamine platinichloride.

Furfurylidenetetramethyldiamine, $C_4H_3O\cdot CH(NMe_2)_2$, formed by the action of dimethylamine on furfuraldehyde, without cooling, is a liquid with a strongly ammoniacal odour. The *platinichloride*,

$$C_9H_{16}ON_2,H_2PtCl_6,$$

is a yellow, crystalline precipitate and decomposes on recrystallisation; the *dimethiodide*, $C_9H_{16}ON_2.2MeI$, forms a yellow, crystalline precipitate and yields an *aurichloride*, $C_4H_3O\cdot CH(NMe_2)_2,2AuCl_4$, which is a yellow, prismatic, crystalline powder and melts at 174°; the *platinichloride* of the dimethochloride crystallises in small rosettes.

G. Y.

Nitration of Methyl Pyromucate. Nitropyromucic Acid. R. MARQUIS (*Bull. Soc. chim.*, 1904, [iii], **31**, 1277—1282. Compare Abstr., 1902, i, 388, 483; 1903, i, 49 and 644).—*Methyl nitropyromucate*,

$$CH\lessdot{}^{C(NO_2)}_{CH-O}\gtrdot C\cdot CO_2Me,$$

prepared by esterifying nitropyromucic acid (Abstr., 1903, i, 49) or by nitrating methyl pyromucate, crystallises in pale yellow lamellæ and melts at 78·5°. *Nitropyromucyl chloride* crystallises in greasy lamellæ and melts at 38°; the *amide*, obtained by the action of dry ammonia on the chloride dissolved in ether, forms silky, white needles and melts at 161°; the *anilide*, similarly prepared, crystallises in lemon-yellow needles and melts at 180°, the p-*toluidide* forms yellow prisms and melts at 162°. Nitropyromucic acid is completely decomposed by the usual oxidising agents, but the ethyl ester is oxidised by sodium dioxide forming fumaric and nitrous acids. T. A. H.

*iso***Pyromucic Acid.** G. CHAVANNE (*Ann. Chim. Phys.*, 1904, [viii], **3**, 507—574).—In addition to the derivatives of *iso*pyromucic acid described in previous papers (compare Abstr., 1901, i, 649; 1902, i, 637, 690; 1903, i, 270; 1904, i, 82), the original contains an account of the preparation and properties of the following derivatives: *iodo*iso*pyromucic acid*, $C_5H_3O_3I$, prepared by the action of iodine and mercuric oxide on *iso*pyromucic acid, crystallises in large, short prisms melting at 150—151° and is soluble in alcohol; by the action of water in sealed tubes at 175° on *iso*pyromucic acid, two *compounds* having the composition $C_9H_6O_3$ are obtained, melting at 186° and 155—160° respectively; the *compound* $C_5H_4O_4Br_2$, obtained by the action of bromine water at 0° on bromo*iso*pyromucic acid, is sparingly soluble in cold water, soluble in alcohol, acetone, or boiling ether, chloroform or benzene; the *compound* $C_4H_2O_2Br_2$ (probably *dibromomaleic dialdehyde*, CHO·CBr⁚CBr·CHO), obtained by the action of excess of bromine on *iso*pyromucic acid at 60°, boils at 132° under 15 mm. pressure, forms large crystals melting at 34°, and is converted quantitatively into mucobromic acid, CHO·CBr⁚CBr·CO_2H, on warming with bromine water. The author suggests the following constitutional formula for *iso*pyromucic acid, $CH\lessdot{}^{CH=CH}_{C(OH)\cdot CO}\gtrdot O$.

M. A. W.

Compounds of Dimethylpyrone with Trichloroacetic Acid. WLADIMIR A. PLOTNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 1088—1091).—Dimethylpyrone forms two compounds with trichloroacetic acid: (1) the *normal* salt, $C_7H_8O_2,CCl_3\cdot CO_2H$, which melts at $45\frac{3}{4}$—$46\frac{1}{2}$°, and (2) the *acid* salt, $C_7H_8O_2,2CCl_3\cdot CO_2H$, which melts at $66\frac{1}{2}$—$67\frac{1}{2}$°. T. H. P.

7 : 2′-Dihydroxyflavonol. STANISLAUS VON KOSTANECKI and A. VON SZLAGIER (*Ber.*, 1904, **37**, 4155—4158. Compare Abstr., 1904, i, 441, 442, 608).—The conclusion of Kostanecki and Katschalowsky (Abstr., 1904, i, 608) with reference to the tinctorial properties of the dihydroxyflavonols is found to be erroneous, owing to the widely

differing solubilities of the isomerides. When tested under similar conditions, the less soluble compounds being employed in the form of paste, the 6 : 2′-, 6 : 3′-, 6 : 4′-, 7 : 2′-, 7 : 3′-, and 7 : 4′-dihydroxyflavonols are all found to dye cotton mordanted with alumina. The *anchi*-position of the hydroxyl groups is therefore without influence on the tinctorial properties.

2′-*Hydroxy*-4′ : 2-*dimethoxychalkone*,

$$OMe\cdot C_6H_3(OH)\cdot CO\cdot CH{:}CH\cdot C_6H_4\cdot OMe,$$

prepared by condensing salicylaldehyde methyl ether with paeonol, crystallises from alcohol in deep yellow needles melting at 94° and dissolves in concentrated sulphuric acid to an orange solution. Boiling with dilute hydrochloric acid and alcohol converts it into 7 : 2′-*dimethoxyflavanone*, $\begin{array}{l} C(OMe){:}CH\cdot C{-}O\cdot CH\cdot C_6H_4\cdot OMe \\ CH{=}CH{-}C\cdot CO\cdot CH_2 \end{array}$, which forms colourless, prismatic needles melting at 102° and dissolving in concentrated sulphuric acid or alcoholic sodium hydroxide to yellow solutions. Its 3-iso*nitroso*-derivative, prepared by the action of amyl nitrite and hydrochloric acid, forms white tablets and melts and decomposes at 195°.

7 : 2′-*Dimethoxyflavonol*, prepared by the hydrolysis of the *iso*nitroso-compound, forms bright yellow, striated tablets and melts at 203°. It forms a sparingly soluble *sodium* salt and dissolves in concentrated sulphuric acid to a yellow solution which shows a bright blue fluorescence after dilution. The *acetyl* derivative forms short, glistening prisms and melts at 138—139°.

7 : 2′-*Dihydroxyflavonol*, $\begin{array}{l} C(OH){:}CH\cdot C{-}O\cdot C\cdot C_6H_4\cdot OH \\ CH{=}CH\cdot C\cdot CO\cdot C\cdot OH \end{array}$, prepared by boiling the dimethoxy-compound with concentrated hydriodic acid, forms yellowish-white needles melting at 271° and dissolves in dilute sodium hydroxide to a pale yellow solution with strong green fluorescence. The solution in concentrated sulphuric acid is pale yellow, and shows a strong blue fluorescence on dilution. C. H. D.

7 : 3′-Dihydroxyflavonol. Stanislaus von Kostanecki and A. Widmer (*Ber.*, 1904, **37**, 4159—4161).—2′-*Hydroxy*-4′ : 3-*dimethoxychalkone*, prepared from *m*-methoxybenzaldehyde and paeonol, crystallises from alcohol in yellow prisms and melts at 80—81°; its *acetyl* derivative forms pale yellow leaflets melting at 70—71°. Warming with dilute sulphuric acid and alcohol converts it into 7 : 3′-*dimethoxyflavanone*, crystallising in white needles melting at 104°. The 3-iso*nitroso*-derivative forms small, pale yellow prisms and melts and decomposes at 160°.

7 : 3′-*Dimethoxyflavonol* crystallises from alcohol in almost colourless needles and melts at 170°. It forms a yellow, sparingly soluble *sodium* salt, and dissolves in concentrated sulphuric acid to a pale yellow solution with green fluorescence. The *acetyl* derivative forms colourless needles melting at 165°.

7 : 3′-*Dihydroxyflavonol* forms white needles melting at 298—300°, and dissolves in dilute sodium hydroxide to a bright yellow solution

with slight green fluorescence. *Acetyl*-7 : 3′-*diacetoxyflavonol*,

$C_{15}H_7O_2(OAc)_3$,

forms white needles and melts at 169°. C. H. D.

7 : 4′-Dihydroxyflavonol. K. Juppen and Stanislaus von Kostanecki (*Ber.*, 1904, **37**, 4161—4163).—7 : 4′-*Dimethoxyflavanone*, obtained from 2′-hydroxy-4′ : 4-dimethoxychalkone (Kostanecki and Osius, Abstr., 1899, i, 370), forms colourless needles melting at 94—95°. Its 3-iso*nitroso*-derivative crystallises from benzene in groups of small prisms and melts and decomposes at 170°.

7 : 4′-*Dimethoxyflavonol* forms bright yellow crystals, melts at 196—197°, and dissolves sparingly in alcohol. Its solution in concentrated sulphuric acid is yellow and shows an intense green fluorescence. The *acetyl* derivative forms colourless tablets melting at 193—194°.

7 : 4′-*Dihydroxyflavonol* crystallises from dilute alcohol in bright yellow needles melting at 310°. It dissolves in dilute sodium hydroxide to a yellow solution with green fluorescence. Its *triacetyl* derivative forms white needles melting at 153°. C. H. D.

[New Alkaloid in] Earth-nut. W. Mooser (*Landw. Versuchs-Stat.*, 1904, **60**, 321—346).—Earth-nut meal contains, in addition to the bases choline and betaine, isolated by Schulze, an alkaloid *arachine*, $C_5H_{14}ON_2$. It was obtained as a yellowish-green syrup, rather readily soluble in water and alcohol, less so in chloroform, and insoluble in light petroleum or ether. The *platinichloride*,

$(C_5H_{13}ON_2)_2,H_2PtCl_6$,

is an orange-coloured, crystalline substance melting at 216°, soluble in cold water and insoluble in hot water. The *aurichloride*,

$(C_5H_{13}ON_2),HAuCl_4$,

forms lemon-coloured, strongly refractive crystals. Both double salts crystallise in a variety of forms.

Subcutaneous injection of arachine hydrochloride immediately produced somnolence with frogs and rabbits, and partial paralysis. In the case of frogs, cutting off the toes produced no movement. The effect of the poison passed off the next day.

A number of samples of earth-nut meal were examined and all were found to contain the alkaloid. N. H. J. M.

Quaternary Ammonium Compounds of the Alkaloids. Max Scholtz and K. Bode (*Arch. Pharm.*, 1904, **242**, 568—574).—Whereas 1-alkyl derivatives of coniine and of conhydrine yield two isomeric additive products with an alkyl haloid containing a different alkyl group (Abstr., 1904, i, 1044), the alkaloids detailed below yield only one additive product in each case; the numbers quoted are melting points.

Brucine with *benzyl bromide*. *Strychnine* with *benzyl bromide*; with *methyl iodoacetate* (240°). *Cinchonine* with *methyl iodoacetate* (200°). *Nicotine* with *benzyl iodide* (2 mols.) (214—215°). *Tropine* with *methyl iodoacetate* (212°); with *benzyl iodide* (236°). *Atropine* with *benzyl bromide* (215°). C. F. B.

Constitution of Ricinine. LÉON MAQUENNE and LOUIS PHILIPPE (*Compt. rend.*, 1904, **139**, 840—843. Compare Abstr., 1904, i, 339).—The hydroxymethylpyridone obtained by the successive action of potassium hydroxide and fuming hydrochloric acid on ricinine has feebly basic properties, forming a crystalline hydrochloride, phosphate, and platinichloride, and it behaves as a monobasic acid towards phenolphthalein. It readily yields substituted derivatives by the action of bromine, and the *compounds* $C_6H_6O_2NBr$, $C_6H_5O_2NBr_2$, and $C_6H_3O_2NBr_4$ are crystalline, soluble in alcohol, and much more strongly acidic than the original compound. The *nitro*-derivative, $C_6H_6O_2N(NO_2)$, crystallises in yellow needles and forms well-defined salts; the *calcium* salt, $(C_6H_5O_4N_2)_2Ca,5H_2O$, crystallises in thin needles and the *ammonium* and *potassium* salts are also crystalline. Phosphorus pentachloride at 160° reacts with hydroxymethylpyridone to form two chlorinated derivatives, of which the one formed in the larger quantity is a *dichloropyridine*, $C_5H_3NCl_2$, boiling at 98° under 18 mm. pressure and reduced by hydrogen iodide and red phosphorus at 170° to pyridine. Hydroxymethylpyridone and ricinine are therefore derivatives of a hydropyridine in which the methyl group is attached to the nitrogen, as represented in the following formulæ :

$$NMe<\begin{matrix}CH{=\!=}CH\\CH{:}C(OH)\end{matrix}>CO \qquad NMe<\begin{matrix}C(CO_2Me){:}C\\ CH{=}CH\cdot C\end{matrix}>N$$

Hydroxymethylpyridone. Ricinine.

M. A. W.

The Development of the Chemistry of Pyrrole in the Last Twenty-five Years. GIACOMO L. CIAMICIAN (*Ber.*, 1904, **37**, 4200—4255).—A lecture delivered before the German Chemical Society. C. H. D.

2:6-Tetramethylpiperidine. ANTOINE P. N. FRANCHIMONT and H. FRIEDMANN (*Proc. k. Akad. Wetensch. Amsterdam*, 1904, **7**, 270—271).—2 : 2 : 6: 6-Tetramethylpiperidine, prepared by the reduction of 3-bromo-2 : 2 : 6 : 6-tetramethylpiperidine by the zinc-copper couple, has the sp. gr. 0·8367 and boils at 155·5—156·5° under 760 mm. pressure. With water, it forms a crystalline *compound* which melts at 28°. The *hydrochloride* and *hydrobromide* sublime, the *hydrogen sulphate* melts at 174° and the *normal sulphate* at 270°. The base reacts very slowly with acid chlorides. Its *methylurethane* has the sp. gr. 0·9848 and boils at 227° under 760 mm. pressure; its *benzoyl* derivative melts at 41—42° and its *picrate* at 225°. A. McK.

***o*-Thymotinpiperidide.** HERMANN HILDEBRANDT (*Ber.*, 1904, **37**, 4456—4458. Compare Abstr., 1900, ii, 676; Kobek, Abstr., 1884, 56; Manasse, Abstr., 1894, i, 577; 1903, i, 28).—On administering thymotic alcohol to rabbits and treating their urine with hydrochloric acid and sodium hypochlorite, there is obtained *dichlorothymotinglycuronic anhydride*, $C_{17}H_{18}O_8Cl_2$, which melts at 80°. The *base*, $C_{17}H_{25}ON$, obtained by warming thymotic alcohol with piperidine and formaldehyde, melts at 140°, and when administered to rabbits appears

in the urine as the same glycuronic acid compound (m. p. 192°) as is obtained from *p*-thymotinpiperidide. This, on hydrolysis with 6—8 per cent. sulphuric acid, yields *o-thymotinpiperidide*, $C_{16}H_{25}ON$, which melts at 141°, gives the thymol reaction when boiled with glacial acetic and sulphuric acids, and is converted into a glycuronic acid compound when administered to rabbits. G. Y.

2-Methyldihydroindole. JULIUS VON BRAUN and A. STEINDORFF (*Ber.*, 1904, **37**, 4581—4584).—Benzoylmethyldihydroindole, when heated to 150—160° with phosphorus pentachloride, is converted into the *imide-chloride*, $CPhCl{:}N{\cdot}C_6H_4{\cdot}CH_2{\cdot}CHMeCl$, of which the benzoyl compound, obtained on hydrolysis, *benzoyl-o-β-chloropropylanilide*, $C_6H_5{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CHClMe$, was isolated. This crystallises in long, colourless needles melting at 130—131°.

The *benzenesulphonyl* derivative, $C_6H_4{<}{}^{\textstyle -CH_2-}_{\textstyle N(SO_2Ph)}{>}CHMe$, is well suited to characterise methyldihydroindole; it separates in glassy, glistening crystals melting at 90°. E. F. A.

Constitution of Ethyl 6:8-Dinitrotetrahydroquinoline-1-carboxylate. G. C. A. VAN DORP (*Rec. Trav. Chim.*, 1904, **23**, 301—323).—*Ethyl tetrahydroquinoline-1-carboxylate*, prepared by the action of ethyl chlorocarbonate on tetrahydroquinoline, is a colourless, highly refractive liquid, which solidifies when cooled and then melts at 27° and boils at 168·5° under 12 mm. or at 181° under 25 mm. pressure. When treated in acetic acid solution with anhydrous nitric acid, it furnishes *ethyl 6(?)-nitrotetrahydroquinoline-1-carboxylate*; this crystallises from alcohol in colourless needles, melts at 78·5°, and by sodium ethoxide is converted into the corresponding nitrotetrahydroquinoline, which melts at 159° (compare Stoermer and Dragendorff, Abstr., 1899, i, 45). *Ethyl 6:8-dinitrotetrahydroquinoline-1-carboxylate*, prepared by adding the ester to anhydrous nitric acid cooled to −5°, crystallises from alcohol in small, faintly yellow plates, melts at 97·5°, and is not acted on by aqueous solutions of potassium hydroxide, but, with sodium ethoxide dissolved in cold alcohol or when heated at 90° with dilute sulphuric acid, yields the corresponding dinitrotetrahydroquinoline, which melts at 164° (compare Simon Thomas, Abstr., 1892, 725), and on oxidation furnishes 6:8-dinitroquinoline.

When ethyl 6:8-dinitrotetrahydroquinoline-1-carboxylate is oxidised with chromic acid, *β-3:5-dinitro-2-aminocarbethoxyphenylpropionic acid* and 3:5-dinitro-2-aminobenzoic acid (m. p. 268°) are produced; the former crystallises in colourless needles, melts and decomposes at 211°, dissolves in alcohol and mineral acids, and is reprecipitated on addition of water. When boiled with an aqueous solution of potassium hydroxide, it resinifies and gives off ammonia. The *ethyl* ester crystallises in needles from a mixture of acetone and water or from alcohol and melts at 134·5°. The free acid, when dissolved in alcohol and heated with sulphuric acid, yields *6:8-dinitro-2-ketotetrahydroquinoline*, which is crystalline and melts at 177°; when boiled with aqueous potash, this furnishes Zwenger's dinitromelilotic acid, β-3:5-dinitro-2-hydroxyphenylpropionic acid.

Methyl tetrahydroquinoline-1-carboxylate forms yellow crystals, melts at 33°, and boils at 172° under 13 mm. pressure; the corresponding 6 : 8-dinitro-derivative melts at 180·5—181°. 1-Phenylsulphonetetrahydroquinoline melts at 64·5—65°, and its 6 : 8-dinitro-derivative crystallises from benzene and melts at 215° (compare Schotten and Schlömann, Abstr., 1892, 351).

Methyl 2-methyltetrahydroquinoline-1-carboxylate, prepared by the action of methyl chlorocarbonate on quinaldine, melts at 42·5° and boils at 239—240°.

1-Phenylsulphone-2-methyltetrahydroquinoline forms colourless crystals from alcohol and melts at 109·5° to 110°. T. A. H.

Derivatives of Chrysene. CARL GRAEBE (*Annalen*, 1904, **335**, 122—138. Compare Abstr., 1900, i, 505; this vol., i, 60).—Chrysodiphen-2′-amic acid, $CO_2H\cdot C_{10}H_6\cdot C_6H_4\cdot CO\cdot NH_2$, which melts at 220°, does not form an ester when treated with methyl alcohol and hydrogen chloride; when heated with concentrated hydrochloric acid at 150°, it is hydrolysed to chrysodiphenic acid. The isomeric amic acid, $NH_2\cdot CO\cdot C_{10}H_6\cdot C_6H_4\cdot CO_2H$, is not found to melt at 275°; it is not hydrolysed by hydrochloric acid at 150°; with methyl alcohol and hydrogen chloride, it forms a *methyl* ester which melts at 170°.

a-Naphthaphenanthridone, $\begin{array}{l}C_{10}H_6\cdot NH\\ |\qquad\ \ |\\ C_6H_4-CO\end{array}$, formed from chrysodiphen-1-amic acid by the action of sodium hypochlorite in aqueous sodium hydroxide solution, melts at 332·5°, sublimes, and dissolves in concentrated sulphuric acid to a colourless solution with slight blue fluorescence. When heated with zinc dust, it yields a *naphthaphenanthridine*, $\begin{array}{l}C_{10}H_6\cdot N\\ |\qquad\ \ \|\\ C_6H_4-CH\end{array}$, which crystallises in colourless leaflets, melts at 135·5° (corr.), and dissolves in concentrated sulphuric acid to a colourless solution with a blue fluorescence; the *hydrochloride*, $C_{17}H_{11}N,HCl,H_2O$, melts and decomposes at 235°; the *aurichloride* melts at 218°; the *mercurichloride* melts at 258°; the *picrate* melts and decomposes at 256°.

β-Naphthaphenanthridone, $\begin{array}{l}C_{10}H_6\cdot CO\\ |\qquad\ \ |\\ C_6H_4-NH\end{array}$, obtained from chrysodiphen-2′-amic acid, melts at 338°. *β-Naphthaphenanthridine*, $\begin{array}{l}C_{10}H_6\cdot CH\\ |\qquad\ \ \|\\ C_6H_4-N\end{array}$, crystallises in colourless leaflets and melts at 182°; the *hydrochloride*, $C_{17}H_{11}N,HCl$, melts at 220°.

β-Chrysenic acid (2-phenylnaphthalene-1-carboxylic acid),

$$C_{10}H_6Ph\cdot CO_2H$$

(Graebe, Abstr., 1900, i, 296), yields chrysoketone when treated with concentrated sulphuric acid; the *silver* salt, $C_{17}H_{11}O_2Ag$, is insoluble in water; the *methyl* ester, $C_{18}H_{14}O_2$, obtained by the action of methyl iodide on the silver salt, melts at 75° and is only very slightly hydrolysed by boiling alcoholic sodium hydroxide; no amide is formed when the acid is treated with phosphorus pentachloride and ammonia.

The *oxime*, $\begin{array}{l}C_{10}H_6\\ |\\ C_6H_4\end{array}\!\!>C{:}N\cdot OH$, prepared from specimens of chrysoketone obtained by different processes, melts and decomposes at 202°.

Chrysofluorene, $\genfrac{}{}{0pt}{}{C_{10}H_6}{C_6H_4}\!\!>\!CH_2$, is best prepared from the ketone in small quantities by heating with zinc dust, and in larger quantities by boiling with 50 per cent. hydriodic acid and red phosphorus. It boils at 413°, is easily soluble in hot benzene or chloroform, and is oxidised to chrysoketone by sodium dichromate in glacial acetic acid solution; the picrate, $C_{17}H_{12},2C_6H_3O_7N_3$, forms orange-red crystals and melts at 127·5°.

Dinaphthylenediphenylene-ethylene, $\genfrac{}{}{0pt}{}{C_{10}H_6}{C_6H_4}\!\!>\!C\!:\!C\!<\!\!\genfrac{}{}{0pt}{}{C_{10}H_6}{C_6H_4}$, formed when chrysofluorene is heated with lead oxide at 320—330° or distilled with lead oxide under reduced pressure, melts at 180—190°, forms intensely red solutions, and yields, with bromine, a colourless *additive* compound; a colourless *hydrocarbon* (*dinaphthylenediphenylene-ethane*?), which melts at 257°, is formed along with the ethylene by the action of lead oxide on chrysofluorene. G. Y.

Chromophorous Groups. II. Methineammonium Dyes. Hans Rupe and Georg L. M. Schwarz (*Zeit. Farb. Text.-Ind.*, 1904, 397—402).—The following thiazoles are analogous to the iminazole-dyes described in a previous paper (Rupe and Porai-Koschitz, Abstr., 1904, i, 107).

2-*Styryl-β-naphthathiazole* (*benzylidene-2-methyl-β-naphthathiazole*),

$$C_{10}H_6<\genfrac{}{}{0pt}{}{S}{N}>C\cdot CH\!:\!CHPh,$$

prepared by heating 2-methyl-β-naphthathiazole with benzaldehyde and zinc chloride at 160—170°, crystallises from glacial acetic acid in white needles and melts at 148—149°. 2-o-*Chlorostyryl-β-naphthathiazole* crystallises from pyridine and melts at 158°. 2-o-*Nitrostyryl-β-naphthathiazole* crystallises from glacial acetic acid or from pyridine in yellow needles, melts at 183°, and on reduction in alcoholic solution with stannous chloride and hydrochloric acid gives 2-o-*aminostyryl-β-naphthathiazole*, which crystallises from pyridine and melts at 225°; the *hydrochloride* of this base dyes mordanted cotton and probably has the quinonoid structure,

$$C_{10}H_6<\genfrac{}{}{0pt}{}{S}{N}>C\cdot CH_2\cdot CH\!:\!C_6H_4\!:\!NH_2Cl$$

(compare *loc. cit.*). 2-o-*Acetylaminostyryl-β-naphthathiazole* crystallises from alcohol and melts at 249°.

2-m-*Nitrostyryl-β-naphthathiazole*, prepared by means of *m*-nitrobenzaldehyde, crystallises from glacial acetic acid in yellow needles and melts at 200°. 2-m-*Aminostyryl-β-naphthathiazole* forms yellow leaflets, melts at 194°, is without tinctorial properties, and therefore probably has the structure $C_{10}H_6<\genfrac{}{}{0pt}{}{S}{N}>C\cdot CH\!:\!CH\cdot C_6H_4\cdot NH_2,HCl$; its *acetyl* derivative forms yellow needles and melts at 215°. 2-p-*Nitrostyryl-β-naphthathiazole* forms orange-yellow needles and melts at 228°. The p-*amino*-compound is a yellow, crystalline powder melting at 245°; its *acetyl* derivative crystallises from glacial acetic acid in white needles and melts at 223°.

2-*Dimethyl*-p-*aminostyryl-β-naphthathiazole*, prepared by means of

p-aminobenzaldehyde, forms bright yellow crystals, melts at 212°, and gives a *dihydrochloride* which is hydrolysed by water to form the base; it has marked tinctorial properties.

2 o-*Hydroxystyryl-β-naphthathiazole*, obtained from salicylaldehyde, crystallises from pyridine and melts at 249°. 2-p-*Hydroxystyryl-β-naphthathiazole* melts at 271° and gives an *acetyl* derivative melting at 159°.

The following compounds were prepared from 2-methyl-α-naphthathiazole. 2-o-*Chlorostyryl α-naphthathiazole* crystallises from pyridine in yellow needles and melts at 144°. 2-o-*Nitrostyryl-α-naphthathiazole* is similar and melts at 168°. 2-o-*Aminostyryl-α-naphthathiazole* crystallises from pyridine or amyl alcohol in yellow leaflets and melts at 185°; its *acetyl* derivative crystallises from alcohol in yellow needles melting at 238°.

2-m-*Nitrostyryl-α-napththathiazole* melts at 190°; 2-m-*aminostyryl-α-naphthathiazole* forms yellow needles, melts at 152°, and gives salts which are colourless; its *acetyl* derivative melts at 242°.

2-p-*Nitrostyryl-α-naphthathiazole* forms lustrous needles and melts at 226°. 2 p-*Aminostyryl-α-naphthathiazole* crystallises in yellow needles and forms a deep red *hydrochloride;* the *acetyl* derivative melts at 218°.

W. A. D.

Formation of Chains. LX. Reactions of the Benzylanilide of α-Bromopropionic Acid and of Di-α-monobromopropionyldiphenylethylenediamine. Carl A. Bischoff and, in part, with Fröhlich, Jackowlew, Kissin, Mazaraki, Milewski, and Pildon (*Ber.*, 1904, **37**, 4341—4350. Compare Abstr., 1901, i, 524—528).—The condensation of the benzanilide of α-bromopropionic acid with the sodium derivatives of phenol, *o*-cresol, thymol, and carvacrol has been studied in benzene, toluene, and xylene solutions in order to determine whether the presence of ortho-methyl or *iso*propyl groups had a retarding or disturbing effect. No such effect could be detected as the yields in the different cases were much the same. In all cases the reaction was normal and no acrylic acid derivatives were obtained. o-*Tolyloxypropionylbenzylaniline*, $C_6H_4Me{\cdot}O{\cdot}CHMe{\cdot}CO{\cdot}NPh{\cdot}CH_2Ph$, crystallises in large, rhombic plates melting at 60—61°. The corresponding *thymoxy*-compound forms colourless triclinic plates melting at 52° and readily soluble in all solvents, and the *carvacroxy*-compound crystallises in compact, monoclinic prisms melting at 60—61°.

The reactions between the sodium derivatives of phenol and of α- and β-naphthols and halogen derivatives of the type

$$BrC(a,b){\cdot}CO{\cdot}NX{\cdot}CH_2{\cdot}CH_2{\cdot}NX{\cdot}CO{\cdot}C(a,b)Br$$

have been studied. The reaction is termed normal when the product is of the type $Z{\cdot}O{\cdot}C(a,b){\cdot}CO{\cdot}NX{\cdot}CH_2{\cdot}CH_2{\cdot}NX{\cdot}CO{\cdot}C(a,b){\cdot}O{\cdot}Z$ (where $Z = C_6H_5$ or $C_{10}H_7$), and abnormal when the products are an unsaturated compound, $C_nH_{2n-1}{\cdot}CO{\cdot}NX{\cdot}CH_2{\cdot}CH_2{\cdot}NX{\cdot}CO{\cdot}C_nH_{2n-1}$, and a phenol, $2Z{\cdot}OH$. The extent to which the abnormal reaction proceeded was determined by extracting the phenol with sodium hydroxide and estimating the free phenol.

The reaction between di-α-bromopropionyldiphenylethylenediamine (compare Abstr., 1893, i, 78) and the sodium derivatives of phenol,

o-cresol, α-naphthol, β-naphthol, ethyl salicylate, and ethyl malonate in benzene, toluene, or xylene solutions is of the normal type and is practically complete after boiling for some 20 hours.

Diphenoxy-α-dipropionyldiphenylethylenediamine,
$C_2H_4(NPh{\cdot}CO{\cdot}CHMe{\cdot}OPh)_2$,
crystallises in glistening needles sparingly soluble in hot light petroleum. The corresponding *di-*o*-tolyloxy-* and *di-*p*-tolyloxy-*compounds have not been obtained in a crystalline form. The *di-α-naphthoxy-*derivative, $C_2H_4(NPh{\cdot}CO{\cdot}CHMe{\cdot}O{\cdot}C_{10}H_7)_2$, crystallises from alcohol in colourless needles melting at 155° and is only sparingly soluble in ether, light petroleum, or cold alcohol. The isomeric *β-naphthoxy-*derivative melts at 90—94°.

The *compound* obtained from the sodium derivative of ethyl salicylate, $C_2H_4(NPh{\cdot}CO{\cdot}CHMe{\cdot}O{\cdot}C_6H_4{\cdot}CO_2Et)_2$, crystallises from methyl alcohol in compact needles melting at 141° and is insoluble in ether or light petroleum. When hydrolysed with alcoholic potash and acidified, the corresponding *acid*, $C_{34}H_{32}O_8N_2$, is obtained. This crystallises from glacial acetic acid in colourless prisms melting at 276° and is insoluble in most solvents.

Dicarbethoxymethylsuccindiphenylethylenediamide,
$C_2H_4[NPh{\cdot}CO{\cdot}CHMe{\cdot}CH(CO_2Et)_2]_2$,
obtained from ethyl sodiomalonate, crystallises in colourless plates, melts at 166°, and is only sparingly soluble in ether or light petroleum.

J. J. S.

Formation of Chains. LXI. Reactions with Di-α-propionylditolylethylenediamine. CARL A. BISCHOFF (MATZ and VON WODZINSKY) (*Ber.*, 1904, **37**, 4350—4355. Compare preceding abstract).—The reaction between α-bromopropionyldi-*p*-tolylethylenediamine and the sodium derivatives of phenol α- and β-naphthols is perfectly normal, and, after 20 hours, some 90—99 per cent. of sodium bromide is formed. The *diphenoxy-*derivative, $C_2H_4[N(C_6H_4Me){\cdot}CO{\cdot}CHMe{\cdot}OPh]_2$, forms colourless crystals melting at 130°; an *isomeride*, melting at 101—102°, has also been obtained. The *di-α-naphthoxy-*derivative melts at 50—52°, and the reaction is practically normal, only some 4 per cent. of free naphthol being formed. The *di-β-naphthoxy-*compound crystallises from dilute alcohol in needles melting and decomposing at 90—91°, and seems to consist of a mixture of two substances melting respectively at 89° and 92—95°.

α-Bromopropionyldi-*o*-tolylethylenediamine condenses with the same sodium salts, but the reaction proceeds more slowly owing to the presence of the *o*-methyl groups, and is to a certain extent abnormal. The *diphenoxy-*derivative crystallises in microscopic, six-sided prisms melting at 137—138°. The *di-α-naphthoxy-*compound melts at 153—154° and the *di-β-naphthoxy-*derivative at 195—196°. The yields of free phenols were: phenol 4, α-naphthol 12, and β-naphthol 8 per cent.

J. J. S.

Formation of Chains. LXII. Reactions of Di-α-bromopropionyldinaphthylethylenediamine. CARL A. BISCHOFF (*Ber.*, 1904, **37**, 4356—4362. Compare preceding abstracts).—[With SCHTSCHEGOLEW.]—Di-α-bromopropionyldi-α-naphthylethylenediamine (Abstr., 1893,

i, 98) condenses with the sodium derivatives of phenols, but the reaction is to a certain extent abnormal. The *diphenoxy*-derivative appears to exist in two isomeric forms, the one sintering at 218° and melting at 223°, and the other melting at 192°. The yield of free phenol was 12 per cent. The *di-α-naphthoxy*-derivative has only been obtained in the form of an amorphous mass melting at about 80°. The yield of α-naphthol was 13 per cent. The *di-β-naphthoxy*-derivative crystallises in four-sided plates and melts at 204°. The yield of free naphthol was about 10 per cent.

[With Soloweitschik.]—The corresponding reactions with the isomeric di-α-bromopropionyldi-β-naphthylethylenediamine have been studied. *Diphenoxy-α-propionyldi-β-naphthylethylenediamine*, after recrystallisation from acetic acid and ethyl acetate, forms microscopic, rhombohedral crystals sintering at 185° and melting at 192—193°. The corresponding *di-α-naphthoxy*-derivative has only been obtained in an amorphous state, but the isomeric *di-β-naphthoxy*-compound crystallises in glistening needles melting at 182°. It is but sparingly soluble in ether, light petroleum, or alcohol, but dissolves readily in chloroform. The yields of free phenols were respectively 4, 7, and 4 per cent., indicating that the reactions were practically normal. Pure di-α-naphthylethylenediamine melts at 133—134° (compare Abstr., 1890, 1333).

J. J. S.

Formation of Chains. LXIII and LXIV. Reactions of Di-α-monobromobutyryldiarylethylenediamines and of Di-α-monobromo*iso*butyryldiarylethylenediamines. Carl A. Bischoff and, in part, with von Berent, Fränkel, Jasinsky, Lanin, Mironenko, Peschudow, Stein, Tobilewitsch, Trozki, Winokurow, and Wulffius (*Ber.*, 1904, **37**, 4548—4556, 4556—4570. Compare Abstr., 1901, i, 524—528, and preceding abstracts).—The reactions between the following ethylenediamine derivatives (Abstr., 1893, i, 78, 98),

$$CHBrEt\cdot CO\cdot NX\cdot CH_2\cdot CH_2\cdot NX\cdot CO\cdot CHBrEt$$

and $CBrMe_2\cdot CO\cdot NX\cdot CH_2\cdot CH_2\cdot NX\cdot CO\cdot CBrMe_2$ (where X = phenyl, *o*-tolyl, *p*-tolyl, α-naphthyl, or β-naphthyl), and the sodium derivatives of phenol α- and β-naphthols have been studied.

The relative reactivities of the compounds with sodium phenoxide in benzene solution are shown in the following table, where the numbers represent the per cent. of sodium bromide formed after one hour.

X	Propionyl.	Butyryl.	*iso*Butyryl.
Phenyl	54	44	29
p-Tolyl	49	43	27
β-Naphthyl	55	42	22
α-Naphthyl	43	42	19
o-Tolyl	40	39·5	25

The reactions with the butyryl derivatives in all cases led to the formation of a considerable amount of the abnormal products, namely, unsaturated compound and free phenol. This abnormality was the

most pronounced (some 32—50 per cent.) when X = *o*-tolyl or α-naphthyl with both butyl and *iso*butyl compounds. In nearly all cases, over 90 per cent. of the theoretical amount of sodium bromide was obtained by heating for a sufficient length of time.

Di-α-crotonyldiphenylethylenediamine, $C_2H_4(NPh{\cdot}CO{\cdot}CH{:}CHMe)_2$, crystallises from dilute alcohol in glistening needles melting at 174—176°, and only sparingly soluble in light petroleum or ether. It has been obtained by the condensation of di-α-bromobutyryldiphenylethylenediamine with the sodium derivatives of phenol and of α- and β-naphthol; although considerable amounts of the normal products were also formed, they could not be obtained in a crystalline state.

*Di-α-crotonyldi-*o*-tolylethylenediamine* crystallises in colourless needles and melts at 211°, and the isomeric *di-*p*-tolyldiamine* melts at 183°. The *di-α-crotonyldi-α-naphthylethylenediamine*,

$$C_2H_4[N(C_{10}H_7){\cdot}CO{\cdot}CH{:}CHMe]_2,$$

also crystallises in colourless needles, melts at 218°, and is sparingly soluble in methyl alcohol, ether, or light petroleum. The normal condensation products, *di-phenoxybutyryldi-α-naphthylethylenediamine* (melting at 54°) and the corresponding *di-α-naphthoxy-* (melting at 58—60°) and *di-β-naphthoxy-* (melting at 58—60°) derivatives have been isolated.

Di-α-crotonyldi-β-naphthylethylenediamine melts at 208° and dissolves readily in chloroform or benzene. The normal condensation products, *di-phenoxybutyryldi-β-naphthylethylenediamine* (melting at 55—57°) and the corresponding *di-α-naphthoxy-* (melting at 65—67°) and *di-β-naphthoxy*-derivatives (melting at 59—60°), have only been obtained in an amorphous state.

*Di-phenoxy*iso*butyryldiphenylethylenediamine*,

$$C_2H_4(NPh{\cdot}CO{\cdot}CMe_2{\cdot}OPh)_2,$$

crystallises from glacial acetic acid in glistening plates melting at 200—203°. The *di-α-naphthoxy*-derivative was only obtained as a resin, and the *di-β-naphthoxy*-compound as glistening needles melting at 182°.

*Di-methylacryldi-*o*-tolylethylenediamine*,

$$C_2H_4[N(C_6H_4Me){\cdot}CO{\cdot}CMe{:}CH_2]_2,$$

crystallises in glistening needles melting at 131° and readily soluble in acetone, benzene, or chloroform. *Di-β-naphthoxy*iso*butyryldi-*o*-tolylethylenediamine* melts at 206°. *Di-phenoxy*iso*butyryldi-*p*-tolylethylenediamine* crystallises in glistening, monoclinic prisms melting at 171°, the corresponding *di-α-naphthoxy*-compound melts at 195° and the isomeric *di-β-naphthoxy*-derivative at 179°.

Di-methylacryldi-α-naphthylethylenediamine,

$$C_2H_4[N(C_{10}H_7){\cdot}CO{\cdot}CMe{:}CH_2]_2,$$

forms a microscopic, crystalline powder melting at 244—247° and sparingly soluble in most solvents with the exception of chloroform. The corresponding normal condensation products were not obtained in a pure state.

*Di-phenoxy*iso*butyryldi-β-naphthylethylenediamine*,

$$C_2H_4[N(C_{10}H_7){\cdot}CO{\cdot}CMe_2{\cdot}OPh]_2,$$

melts at 192° and the corresponding *di-β-naphthoxy*-derivative at 179°.

Small amounts of other crystalline products have been obtained in several of the reactions, but have not been investigated.

J. J. S.

Bromination of 1 : 5-Diaminoanthraquinone. ROLAND SCHOLL and H. BERBLINGER (*Ber.*, 1904, **37**, 4180—4184).—The bromination of 1 : 5-diaminoanthraquinone proceeds differently according to the presence or absence of water. When the reaction is carried out in glacial acetic acid solution, or when the dry compound is exposed to bromine vapour, products containing a high proportion of bromine are obtained. These are, however, unstable, the excess of bromine being removed by exposure under reduced pressure, or by means of sodium hydrogen sulphite, the product in each case being the dibromo-derivative. The intermediate product appears to be a perbromide (compare Fries, Abstr., 1904, i, 571). On the addition of water to the perbromide, the loosely combined bromine enters the nucleus, forming tetrabromodiaminoanthraquinone. The same compound is obtained when the bromination is carried out from the first in the presence of water.

2 : 6-*Dibromo*-1 : 5-*diaminoanthraquinone* crystallises from nitrobenzene in steel-blue needles and melts at 274°. It dissolves readily in warm concentrated sulphuric acid, the crystalline *sulphate* being precipitated on cooling or slightly diluting the solution. The *tetra-acetyl* derivative forms yellow, prismatic needles which char at about 240°, and dissolves in concentrated nitric acid at 0°, being precipitated unchanged by water. The proof of the orientation given above will form the subject of a later communication.

2 : 4 : 6 : 8-*Tetrabromo*-1 : 5-*diaminoanthraquinone*, prepared as above, crystallises from nitrobenzene in needles resembling the dibromo-compound and melts above 300°. The *tetra-acetyl* derivative forms yellow needles and chars above 220°.

C. H. D.

2 : 3-Diaminoanthraquinone and Azines of the Anthraquinone Series. ROLAND SCHOLL and PHILIPP KAČER (*Ber.*, 1904, **37**, 4531—4534. Compare this vol., i, 70, 102).—2 : 3-*Diaminoanthraquinone*, obtained by the reduction of the 3-nitro-2-amino-derivative (*loc. cit.*) with aqueous sodium sulphide, separates from nitrobenzene in brownish-red crystals which do not melt at 320°. The *sulphate*, $C_6H_4{:}(CO)_2{:}C_6H_2(NH_2,H_2SO_4)_2$, forms a grey, crystalline powder, which is hydrolysed in contact with much water. The *diacetyl* derivative is yellow and crystallises from nitrobenzene.

9′ : 10′-*Phenanthra*-2 : 3-*anthraquinoneazine*,

$$C_6H_4{<}{}^{CO}_{CO}{>}C_6H_2{<}{}^{N}_{N}{>}C_{14}H_8,$$

obtained by condensing 2 : 3-diaminoanthraquinone with phenanthraquinone in acetic acid solution, crystallises from nitrobenzene in compact, yellow needles which do not melt at 320°. It becomes strongly electrified when powdered, dissolves in concentrated sulphuric acid to a carmine-red solution, and does not yield a blue *N*-dihydroazine dye (Abstr., 1904, i, 110) on treatment with alkaline hyposulphite solution.

1′ : 2′-*Naphtha-*2 : 3-*anthraquinoneazine*,

$$C_6H_4<{CO \atop CO}>C_6H_2<{N \atop N}\gg C_{10}H_6,$$

obtained by condensing the diamino-compound with β-naphthaquinone, crystallises from cumene in yellow needles which melt above 320°.

Benzil condenses with the diamino-compound yielding *αβ-diphenyl-2 : 3-anthraquinoxalinequinone*, $C_6H_4<{CO \atop CO}>C_6H_2<{N:CPh \atop N:CPh}$, which crystallises from acetic acid in yellowish-brown needles melting at 271°.

J. J. S.

Action of Phenylhydrazine on Arylthiosulphonated Ethyl Acetoacetates. JULIUS TRÖGER and FRANZ VOLKMER (*J. pr. Chem.*, 1904, [ii], **70**, 375—392. Compare Abstr., 1900, i, 494).—Ethyl arylthiosulphonacetoacetates, $SO_2R\cdot S\cdot CHAc\cdot CO_2Et$, react with phenylhydrazine in warm alcohol or glacial acetic acid solution to form 1-phenyl-3-methylpyrazolone-4-ketophenylhydrazone (Buchka and Sprague, Abstr., 1890, 28), but with phenylhydrazine in ethereal solution they form phenylhydrazones of arylthiosulphonacetoacetylphenylhydrazides, $NHPh\cdot N:CMe\cdot CH(S\cdot SO_2R)\cdot CO\cdot NH\cdot NHPh$. These remain unchanged when boiled with alcohol.

The following new ethyl arylthiosulphonacetoacetates are described: $R = o\text{-}C_7H_7$ is a viscid, yellow oil; $R = 3:4\text{-}C_6H_3Me_2$ is a viscid, brown oil; $R = p\text{-}C_6H_4Cl$ crystallises in rhombic plates and melts at 56—57°; $R = p\text{-}C_6H_4Br$ crystallises in plates and melts at 70—71°; $R = p\text{-}C_6H_4I$ crystallises in colourless needles and melts at 90—91°; $R = p\text{-}C_6H_4(OMe)$ is a viscid, yellow oil.

The following phenylhydrazones of arylthiosulphonacetoacetylphenylhydrazides have been prepared: $R = p\text{-}C_7H_7$ crystallises in white, slender needles or leaflets and melts at 163—164°; $R = o\text{-}C_7H_7$ crystallises in matted, white needles and melts and decomposes at 145—146°; $R = C_6H_5$ crystallises in white needles and melts at 134—135°; $R = \beta\text{-}C_{10}H_7$ forms slender needles or yellow leaflets and melts and decomposes at 156—157°; $R = \alpha\text{-}C_{10}H_7$ crystallises in long, thin needles and melts and decomposes at 139—140°; $R = 3:4\text{-}C_6H_3Me_2$ is a yellow powder and melts and decomposes at 150°; $R = p\text{-}C_6H_4Cl$ is a white, crystalline powder and melts and decomposes at 160—161°; $R = p\text{-}C_6H_4Br$ forms a white, crystalline mass and melts and decomposes at 168—169°; $R = p\text{-}C_6H_4I$ crystallises in slender, white needles and melts and decomposes at 167—168°; $R = p\text{-}C_6H_4(OMe)$ forms a white, crystalline mass and melts and decomposes at 135—136°.

Sodium arylthiosulphonates, required for the preparation of ethyl arylthiosulphonacetoacetates, are best prepared by heating the concentrated aqueous solution of the corresponding sodium arylsulphinates with freshly precipitated sulphur. They are characterised by formation of the crystalline p-phenylenediamine salts.

p-*Phenylenediamine* p-*anisylthiosulphonate*,

$$(OMe\cdot C_6H_4\cdot SO_2\cdot SH)_2,C_6H_8N_2,$$

melts at 161° to a blue liquid. p-*Phenylenediamine* 1 : 3 : 4-*xylylthio-*

sulphonate crystallises in thin leaflets and melts to a blue liquid at 157°. p-*Phenylenediamine* p-*iodophenylthiosulphonate* crystallises in small leaflets and melts at 155—156°. G. Y.

Separation of Aldoses by Secondary Hydrazines. RUDOLF OFNER (*Ber.*, 1904, **37**, 4399—4402. Compare Abstr., 1904, i, 936).—The separation of phenylmethylglucosazone, prepared from dextrose and phenylmethylhydrazine, is assisted by the addition of a nucleus of the same substance prepared from *d*-fructose.

The presence of acetic acid does not prevent the separation of hydrazones. Dextrosephenylmethylhydrazone, xylosephenylmethylhydrazone, and xylosephenylbenzylhydrazone were respectively separated from solutions which contained free acetic acid. A. McK.

The Phenylmethylhydrazine Reaction of Fructose. CARL NEUBERG (*Ber.*, 1904, **37**, 4616—4618).—Dextrose does not yield an osazone by the action of phenylmethylhydrazine according to Ofner's method (Abstr., 1904, i, 936; preceding abstract), whilst *d*-fructose does.

The formation of an osazone, observed by Ofner by the prolonged action of phenylmethylhydrazine on dextrose, is caused possibly by the transformation of dextrose into *d*-fructose as stated by de Bruyn and van Ekenstein. A. McK.

Dimethyl Mesoxalate-phenylhydrazone and its Derivatives. CARL BÜLOW and AUGUST GANGHOFER (*Ber.*, 1904, **37**, 4169—4179. Compare Bülow, Abstr., 1900, i, 56; 1901, i, 98; 1902, i, 325, 649; Eibner, Abstr., 1903, i, 871).—The authors' investigations lead to the conclusion that when an aromatic diazonium compound combines with a fatty compound containing an acid methylene group, the product is an azo-compound in all cases where the ketonic group can change into the enolic group. In all other cases a hydrazone is obtained.

Methyl mesoxalatephenylhydrazone, $NHPh\cdot N\colon C(CO_2Me)_2$, prepared from diazobenzene chloride and methyl malonate, melts at 62° (compare R. Meyer, Abstr., 1891, 922). Ammonia converts it into *mesoxamidephenylhydrazone*, $NHPh\cdot N\colon C(CO\cdot NH_2)_2$, crystallising from acetic acid in yellow needles melting at 231—232°. Methylamine forms *mesoxalobismethylamidephenylhydrazone*,

$$NHPh\cdot N\colon C(CO\cdot NHMe)_2,$$

crystallising from alcohol in yellow needles and melting at 117—118°. It dissolves in alkali hydroxides, thus reacting in the tautomeric form, $CHPh\cdot N\colon C[C(OH)\colon NMe]_2$.

Methyl mesoxalate-o-*carboxyphenylhydrazone*,

$$CO_2H\cdot C_6H_4\cdot NH\cdot N\colon C(CO_2Me)_2,$$

from methyl malonate and diazotised *o*-aminobenzoic acid, crystallises from alcohol in small, yellow needles melting at 186—187°. The *diamide* forms yellow needles melting at 275°; the *bismethylamide* melts at 247°.

Methyl mesoxalate-m-*carboxyphenylhydrazone*, from methyl malonate and diazotised *m*-aminobenzoic acid, crystallises from dilute alcohol in

yellow needles melting at 157—158°. The *diamide* melts above 285° and the *bismethylamide* at 247—248°.

Methyl mesoxalate-p-*carboxyphenylhydrazone* forms yellow needles melting and decomposing at 238°. Boiling sodium hydroxide hydrolyses it to *mesoxalic acid* p-*carboxyphenylhydrazone*, melting and decomposing at 275°. *Mesoxamidephenylhydrazone*-p-*carboxylic acid* forms yellow crystals melting above 285°. The *bismethylamide* melts above 285°.

Methyl mesoxalate-o-*nitrophenylhydrazone*,

$$NO_2\cdot C_6H_4\cdot NH\cdot N\colon C(CO_2Me)_2,$$

from methyl malonate and diazotised *o*-nitroaniline, forms slender needles and melts at 143—144°; the *bismethylamide* melts at 186—187°.

Methyl mesoxalate-m-*nitrophenylhydrazone* melts at 115—116°; the *diamide* forms brownish-yellow crystals and melts at 235°; the *bismethylamide* forms yellow, felted needles and melts at 202—203°.

Methyl mesoxalate-p-*nitrophenylhydrazone* forms yellow needles melting at 162—163°; the *diamide* melts above 285°; the *bismethylamide* forms yellow, felted needles and melts at 243°.

Methyl mesoxalate-o-*tolylhydrazone* forms dark yellow needles melting at 75—76°; the m-*tolylhydrazone* forms yellow crystals melting at 63°; the p-*tolylhydrazone* melts at 89—90°, its *diamide* at 173—174°, and its *bismethylamide* at 91°.

Methyl mesoxalate-o-*anisylhydrazone* forms thick, yellow needles melting at 112—113°, and its *diamide* melts at 143°; the p-*anisylhydrazone* melts at 91°.

Methyl mesoxalate-as-m-*xylylhydrazone* forms slender, yellow needles melting at 93°.

Bülow's reaction (violet coloration with concentrated sulphuric acid and potassium dichromate) is given by those hydrazones which do not contain a para-substituent, except the nitro- and methoxy-derivatives. C. H. D.

[Action of Amyl Nitrite on Phenyl-*m*-nitrobenzylidenehydrazine]. GAETANO MINUNNI (*Gazzetta*, 1904, **34**, ii, 276—280).—According to the author, the compound I of Bamberger and Pemsel (Abstr., 1903, i, 285) is diphenyldi-*m*-nitrobenzylidenehydrotetrazone (Minunni, Abstr., 1898, i, 190), their compound III (given as (2) in the abstract quoted above) being dehydrophenyl-*m*-nitrobenzylidenehydrazone (Abstr., 1898, i, 190) and compound V (given as (4) in the abstract) *iso*dehydrophenyl-*m*-nitrobenzylidenehydrazone (*loc. cit.*). T. H. P.

3:6-Dimethylpyridazine. CARL PAAL and CARL KOCH (*Ber.*, 1904, **37**, 4382—4387. Compare Abstr., 1903, i, 290).—3:6-*Dimethylpyridazine*, $CMe<\begin{matrix}N——N\\ CH\colon CH\end{matrix}>CMe$, prepared either by heating dimethylpyridazinedicarboxylic acid with 5 per cent. hydrochloric acid in sealed tubes at 200°, or by heating the potassium salt of dimethylpyridazinecarboxylic acid, distils without decomposition at 214—215°, or at 109—110° under 20 mm. pressure, and solidifies to a

colourless, hygroscopic, crystalline mass melting in sealed capillary tubes at 32°. The *hydrochloride* crystallises in colourless, flat needles and plates melting at 184°; the *aurichloride*, $C_6H_8N_2,HAuCl_4$, forms yellow needles melting at 170°; the *platinichloride*, $(C_6H_8N_2)_2,H_2PtCl_6$, forms dark reddish-brown crystals decomposing above 200°; the *mercurichloride* from the hydrochloride, $C_6H_8N_2,HCl,2HgCl_2$, separates in needles which melt at 140°, whereas the base forms a *compound*, $C_6H_8N_2,HgCl_2$, melting at 115°; the *picrate* crystallises in yellow, silky, glistening needles melting at 164°.

3 : 6-*Dimethylhexahydropyridazine*, $CHMe<\begin{matrix}NH\text{--}NH\\CH_2\cdot CH_2\end{matrix}>CHMe$, prepared by the reduction of dimethylpyridazine with sodium and alcohol, is a colourless, clear liquid boiling at 180°; the *hydrochloride* crystallises in colourless, concentrically-grouped prisms melting at 164°.

E. F. A.

Condensation of Aminoacetone with Benzaldehyde. THEODOR ALEXANDER (*Monatsh.*, 1904, **25**, 1073—1080. Compare Pomeranz, Abstr., 1894, i, 552).—When shaken in a dilute aqueous solution of sodium hydroxide, aminoacetone and benzaldehyde condense to form the *dihydropyrazine* compound, $CMe<\begin{matrix}N\cdot CH_2\\CH_2\cdot N\end{matrix}>C\cdot CH{:}CHPh$; it is a viscid, yellow liquid which boils at 151° under 10 mm. pressure. The *hydrochloride*, $C_{13}H_{14}N_2,HCl$, is a white, hygroscopic substance; the *platinichloride*, $(C_{13}H_{14}N_2)_2,H_2PtCl_6$, is obtained as an orange-yellow, crystalline precipitate. On reduction with sodium in amyl-alcoholic solution, the condensation product yields the di-acid *base*, $C_{13}H_{20}N_2$, which is a colourless, mobile liquid, has an aromatic odour, and boils at 153° under 11 mm. pressure. The *hydrochloride*, $C_{13}H_{20}N_2,2HCl$, is a white, crystalline, hygroscopic substance.

When heated with water and a few drops of hydrochloric acid in a sealed tube at 180°, the condensation product is decomposed with formation of benzaldehyde. G. Y.

Interaction of Zinc Ethyl and Benzenediazonium Chloride. III. MICHAEL M. TICHWINSKY (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 1052—1055. Compare Abstr., 1903, i, 441, and 1904, i, 268).—Besides the compounds already given as formed in this reaction (*loc. cit.*) there results also:

1-*Ethyl*-2 : 3 : 4-*trihydrocinnoline*, $C_{10}H_4N_2$, which boils at 90—96° under 13 mm. pressure and is soluble in 7 per cent. hydrochloric acid, from which it is precipitated unchanged by the addition of sodium hydroxide.

The author considers that the benzenediazonium chloride is first converted into a hypothetical ethyldiazobenzene, which, under the influence of zinc ethyl, and later of water, combines with the elements of ethane to give phenyldiethylhydrazine, NEtPh·NHEt. The latter then loses 2 atoms of hydrogen with the formation of a second six-carbon ring. T. H. P.

Action of Zinc Ethyl on Phenylazoethane. MICHAEL M. TICHWINSKY (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 1056—1062. Compare preceding abstract).—The action of zinc ethyl on phenylazoethane in ethereal solution yields phenyldiethylhydrazine, $NHPh \cdot NEt_2$, *s*-ethylphenylhydrazine, and 1-ethyl-2 : 3 : 4-trihydrocinnoline.

T. H. P.

An Oxidation Product of Amino-orcinol Mono-methyl Ether. FERDINAND HENRICH and F. SCHIERENBERG (*J. pr. Chem.*, 1904, [ii], **70**, 365—374. Compare Abstr., 1897, i, 446; 1903, i, 414; 1904, i, 494).—When amino-orcinol mono-methyl ether (1 mol.) is dissolved in aqueous potassium hydroxide (2 mols.) and a current of air passed through the solution for a week, the phenoxazine *derivative*, $\begin{array}{l} C\colon CMe{-}C\colon N \cdot C \cdot C(OMe) \cdot CH \\ CO \cdot CH\colon C \cdot O{-}C \cdot C(NH_2) \cdot CMe \end{array}$, is produced. It crystallises in matted, red needles, melts at 256—260°, is easily soluble in warm ethyl acetate, benzene, or glacial acetic acid, and dissolves in concentrated sulphuric acid to a violet solution. When treated with sodium nitrite in dilute hydrochloric acid solution, it forms an intensely blue solution, which, with evolution of gas, deposits a brown, flocculent precipitate. When boiled with alcoholic alkali hydroxides, the phenoxazine derivative is decomposed. The *hydrochloride*, $C_{15}H_{14}O_3N_2,HCl$, crystallises in green leaflets and is hydrolysed by warm water; the *hydrobromide*, $C_{15}H_{14}O_3N_2,HBr$, is green. When heated with aluminium chloride at 210—220°, or with concentrated hydrochloric acid at 200°, the phenoxazine derivative yields methyl chloride and, with the latter, a *product*, $C_{14}H_{12}O_3N_2$ (?), which resembles the archil dyes. The *acetyl* derivative, $C_{15}H_{13}O_3N_2Ac$, crystallises in clusters of yellow needles, decomposes above 265°, and dissolves in concentrated hydrochloric acid to a dark orange-coloured solution, which, on addition of ether, deposits a *hydrochloride*.

Reduction of the phenoxazine derivative with stannous chloride and hydrochloric acid leads to the formation of the *dihydrochloride* of a dihydrophenoxazine compound, $C_{15}H_{16}O_3N_2,2HCl$, which crystallises in white, silky needles, yields the phenoxazine derivative when treated with aqueous alkali hydroxides, dissolves in concentrated sulphuric acid to a bluish-green solution, and gives an intensely blue coloration and a dark red substance when treated with sodium nitrite solution. The *triacetyl* derivative, $C_{15}H_{13}O_3N_2Ac_3$, obtained by the action of acetic anhydride and sodium acetate on the hydrochloride, crystallises in sheaves of red needles, melts at 166—167°, gives a yellow, changing to red, and finally to blue, coloration with concentrated sulphuric acid, and dissolves in concentrated hydrochloric acid to a dark green, in nitric acid to a red solution.

Simultaneous reduction and acetylation of the phenoxazine derivative by means of zinc dust, glacial acetic acid, and acetic anhydride leads to the formation of the *diacetyl* derivative of the dihydrophenoxazine compound, $C_{15}H_{14}O_3N_2Ac_2$, which crystallises in colourless leaflets or sheaves of short needles, melts at 211—212°, is easily soluble in alcohol, chloroform, ethyl acetate, or glacial acetic acid, and

dissolves in concentrated sulphuric acid to a red, changing to a green, and in concentrated hydrochloric acid to a green, changing to a red, solution; with sodium nitrite, it gives an orange coloration.

The action of bromine on the phenoxazine derivative in glacial acetic acid solution leads to the formation of the *bromo*-compound, $C_{15}H_{13}O_3N_2Br$, which melts at 212°. G. Y.

Formation of Heterocyclic Compounds from Hydrazine Derivatives. XV. The Metallic Derivatives of the Condensation Products of Acyl-hydrazines with Aldehydes and Ketones, and their Behaviour towards Acid Chlorides and Iodine. ROBERT STOLLÉ and ED. MÜNCH (*J. pr. Chem.*, 1904, [ii], **70**, 393—422. Compare Abstr., 1903, i, 721; 1904, i, 102, 200, 453, 626, 627, 694, 695, 696, 697).—*Sodium benzoylbenzylidenehydrazine*, CHPh:N·NNaBz, is precipitated as a white powder on addition of ether to the solution of benzoylhydrazine in alcoholic sodium hydroxide; the *silver* derivative, CHPh:N·NAg·Bz, formed on addition of silver nitrate to the solution of benzoylhydrazine and sodium ethoxide (1 mol.) in alcohol, is a white powder, which becomes brown on exposure to light and commences to decompose at 100°; the *mercurichloride* derivative is a white, crystalline powder.

Benzoyl-p-*tolylidenehydrazine*, C_7H_7·CH:N·NHBz, crystallises in colourless, strongly refractive needles and melts at 155°; the *silver* derivative, $C_{15}H_{13}ON_2Ag$, is a white powder which decomposes at 180°.

Benzoylfurfurylidenehydrazine melts at 182° (m. p. 179°; Minunni and Carta-Satta, Abstr., 1900, i, 251); the *silver* derivative is a yellow powder.

The *silver* derivative of acetylbenzylidenehydrazine, $C_9H_9ON_2Ag$, decomposes with evolution of a gas at 227°; the *mercurichloride* derivative, $C_9H_9ON_2$·HgCl, is a white, crystalline powder.

Benzoylethylidenehydrazine, CHMe:N·NHBz, crystallises in glistening leaflets and melts at 162°; when dissolved in an alcoholic solution of 1 mol. of sodium ethoxide and treated with silver nitrate, it yields a white precipitate which rapidly decomposes.

The action of chloral hydrate on benzoylhydrazine in ethereal solution at 35° leads to the formation of an *additive* compound, NHBz·NH·CH(OH)·CCl_3, which is obtained on evaporation of the solution in colourless crystals; it melts at 72° with formation of the *condensation* product, NHBz·N:CH·CCl_3, which is also formed by heating benzoylhydrazine with chloral hydrate on the water-bath. This crystallises in slender needles and melts and decomposes at 194°.

When heated together at 120°, benzoylhydrazine and benzophenone form the *additive* compound, NHBz·NH·CPh_2·OH, which crystallises in colourless, refractive, slender needles, and melts and is converted into the condensation product at 108°.

The *silver* derivative of the condensation product, $C_{20}H_{15}ON_2Ag$, is a yellow powder which is fairly stable towards light; the *mercuric* derivative, $(C_{20}H_{15}ON_2)_2Hg$, crystallises in colourless needles and melts at 241°.

The *sodium* derivative, $C_{16}H_{12}O_2N_4Na_2,2C_2H_6O$, the *silver* derivative, $C_{16}H_{12}O_2N_4Ag_2$, and the *mercuric* derivative, $C_{16}H_{12}O_2N_4Hg,2C_2H_6O$, of dibenzoylglyoxalosazone are described.

The *monosodium* derivative of dibenzoylbenzilosazone, $C_{28}H_{21}O_2N_4Na$, crystallises in glistening needles; the *disodium* derivative,

$$C_{28}H_{20}O_2N_4Na_2,2C_2H_6O,$$

loses $2C_2H_6O$ at 120°; the *monosilver* derivative, the *disilver* derivative, and the *dimercurichloride* derivative, $C_{28}H_{20}O_2N_4(HgCl)_2$, are described.

4-Benzoyl-2 : 5-diphenyl-4 : 5-dihydro-1 : 3 : 4-oxadiazole (Abstr., 1904, i, 102) forms thick, colourless crystals and melts at 138°. When boiled with dilute sulphuric acid, it is hydrolysed to dibenzoylhydrazine and benzaldehyde.

4-Acetyl-2 : 5-diphenyl-4 : 5-dihydro-1 : 3 : 4-oxadiazole crystallises in colourless needles, melts at 98°, and is hydrolysed by dilute acids to benzoylacetylhydrazine and benzaldehyde, which react in warm dilute acids to form benzoylbenzylidenehydrazine and acetic acid.

4-*Benzoyl*-5-*phenyl*-2-*methyl*-4 : 5-*dihydro*-1 : 3 : 4-*oxadiazole* crystallises in large, colourless crystals and melts at 53°. It reduces ammoniacal silver nitrate on prolonged boiling, especially in presence of sodium hydroxide; when boiled with dilute acids, it yields benzoylbenzylidenehydrazine.

4-*Acetyl*-5-*phenyl*-2-*methyl*-4 : 5-*dihydro*-1 : 3 : 4-*oxadiazole* crystallises in slender, white needles, melts at 91°, reduces ammoniacal silver nitrate slowly at the ordinary temperature, and is hydrolysed by very dilute alcoholic hydrochloric acid at the ordinary temperature to diacetylhydrazine and acetylbenzylidenehydrazine, by boiling alcoholic hydrochloric acid to benzaldehyde, hydrazine, and acetic acid.

4-*Benzoyl*-2 : 5 : 5-*triphenyl*-4 : 5-*dihydro*-1 : 3 : 4-*oxadiazole* crystallises in slender, colourless needles and melts at 131°.

Diphenyloxadiazole is formed by the action of iodine on the silver or the mercurichloride derivatives of benzoylbenzylidenehydrazine, or by oxidation of benzoylbenzylidenehydrazine with potassium ferricyanide or amyl nitrite. p-*Tolylphenyl*-1 : 3 : 4-*oxadiazole*, obtained by the action of iodine on benzoyl-*p*-tolylidenehydrazine suspended in ether, crystallises in leaflets and melts at 126°; the *additive* compound, $C_{15}H_{12}ON_2,AgNO_3$, crystallises in white, glistening needles and melts and decomposes at 258°.

Phenylfuryl-1 : 3 : 4-*oxadiazole*, formed by the action of iodine on the silver derivative of benzoylfurfurylidenehydrazine, crystallises in colourless leaflets, melts at 105°, and forms the *additive* compound, $C_{12}H_8O_2N_2,AgNO_3$, which crystallises in soft, white needles and decomposes at 215°.

The action of iodine on the mercuric derivative of benzophenonebenzoylhydrazine in ethereal solution leads to the formation of diphenylketazine and 4-benzoyl-2 : 5 : 5-triphenyl-4 : 5-dihydro-1 : 3 : 4-oxadiazole.

Diphenylbisoxadiazole, $\begin{matrix}N\text{—}N\\ \| \quad \\ CPh\cdot O\end{matrix}\!>\!C\cdot C\!<\!\begin{matrix}N\cdot N\\ \quad \| \\ O\text{–}CPh\end{matrix}$, is formed by the action of iodine on the mercuric derivative of glyoxaldibenzoylosazone in ethereal solution, or by heating dibenzoyloxalylhydrazine with phosphoric oxide. It crystallises in slender, white, glistening needles,

melts at 270°, and is hydrolysed by dilute hydrochloric acid at 150° to benzoic acid and hydrazine hydrochloride. G. Y.

Formation of Heterocyclic Compounds from Hydrazine Derivatives. XVI. Diazoles and Bisdiazoles. ROBERT STOLLÉ and W. KIND (*J. pr. Chem.*, 1904, [ii], 70, 423—432).—When heated with phosphoric oxide, benzoylhydrazine yields 2 : 5-diphenyl-1 : 3 : 4-oxadiazole, 2 : 5-diphenyl-1 : 3 : 4-triazole, and 3 : 6-diphenyl-1 : 4-dihydro-1 : 2 : 4 : 5-tetrazine. When heated with phosphorus pentasulphide in a vacuum at 210°, benzoylhydrazine forms diphenylthiodiazole, $\begin{matrix}N{:}CPh\\ \vert \\ N{:}CPh\end{matrix}{>}S$, which crystallises in glistening scales and melts at 141—142°. It is formed also when benzylidenebenzoylhydrazine or benzylideneazine is heated with phosphorus pentasulphide.

Diacetyloxalylhydrazine, $NHAc{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}NHAc,H_2O$, formed when oxalylhydrazine is heated for one hour at 140° with acetic anhydride, crystallises in glistening, white scales, melts at 276°, is easily soluble in hot water or dilute alkali hydroxides or ammonia, reduces ammoniacal silver nitrate and Fehling's solutions only on prolonged warming, and on prolonged boiling with dilute acids is hydrolysed to acetic and oxalic acids and hydrazine. *Hexa-acetyloxalylhydrazine*, formed when oxalylhydrazine is boiled with acetic anhydride in a reflux apparatus for two days, crystallises in delicate needles, melts at 156—158°, and is hydrolysed to oxalylhydrazine when boiled with water.

Dimethylbisoxadiazole, $\begin{matrix}N\text{—}N\\ \Vert \\ CMe{\cdot}O\end{matrix}{>}C{\cdot}C{<}\begin{matrix}N{\cdot}N\\ \Vert \\ O{\cdot}CMe\end{matrix}$, is formed when diacetyloxalylhydrazine is heated with phosphoric oxide in a vacuum or when hexa-acetyloxalylhydrazine is heated in a vacuum at 180—240°, or when oxalylhydrazine is boiled for two days with acetic anhydride and the product distilled under reduced pressure. It crystallises in slender, colourless needles, melts at 212°, and sublimes without decomposing; the *silver nitrate additive* compound, $C_6H_6O_2N_4,2AgNO_3$, crystallises in needles and melts and decomposes at 215°.

Dimethylbisthiodiazole, $\begin{matrix}N\text{—}N\\ \Vert \\ CMe{\cdot}S\end{matrix}{>}C{\cdot}C{<}\begin{matrix}N{\cdot}N\\ \Vert \\ S\text{—}CMe\end{matrix}$, obtained by heating diacetyloxalylhydrazine with phosphorus pentasulphide at 125—150°, crystallises in colourless, matted needles, melts at about 238°, sublimes without decomposition, and forms an *additive* compound with silver nitrate, $C_6H_6N_4S,2AgNO_3$, which crystallises in silky needles.

Dibenzoyloxalylhydrazine, formed by the action of benzoic chloride and sodium hydroxide on oxalylhydrazine, crystallises in white needles and melts at 278°. When heated with phosphorus pentasulphide in a vacuum at 200°, it yields *diphenylbisthiodiazole*,

$$\begin{matrix}N\text{—}N\\ \Vert \\ CPh{\cdot}S\end{matrix}{>}C{\cdot}C{<}\begin{matrix}N{\cdot}N\\ \Vert \\ S{\cdot}CPh\end{matrix},$$

which forms a loose, white powder, commences to sinter at 245°, and is completely melted at 252°. G. Y.

Formation of Heterocyclic Compounds from Hydrazine Derivatives. XVII. Diphenylosotetrazine and Diphenylosotriazole. ROBERT STOLLÉ, ED. MÜNCH, and W. KIND (*J. pr. Chem.*, 1904, [ii], **70**, 433—441).—2 : 3-*Dibenzoyl*-5 : 6-*diphenyl*-2 : 3-*dihydro*-1 : 2 : 3 : 4-*tetrazine*, $\begin{matrix} CPh{:}N{\cdot}NBz \\ | \quad\quad\ \ | \\ CPh{:}N{\cdot}NBz \end{matrix}$, is formed by the action of iodine on the silver derivative of dibenzoylbenzilosazone in carbon tetrachloride solution, and on the mercurichloride derivative of dibenzoylbenzilosazone suspended in ether, and by the oxidation of benzildibenzoylosazone with potassium ferricyanide and alkaline solution. It crystallises with 1 mol. of alcohol of crystallisation, which is lost at 100° ; when dried at 100° is a white, voluminous powder, and melts at 189°. When boiled with dilute hydrochloric acid in alcoholic solution, it yields 2-*benzoyl*-5 : 6-*diphenyl*-2 : 3-*dihydro*-1 : 2 : 3 : 4-*tetrazine*, which crystallises in slender, colourless needles, melts at 248°, and is soluble in dilute sodium hydroxide or ammonia. The *silver* derivative, $C_{21}H_{15}ON_4Ag$, is an amorphous, yellow powder ; the *mercurichloride* derivative, $C_{21}H_{15}ON_4{\cdot}HgCl$, is a white powder.

When boiled with concentrated hydrochloric acid and alcohol, the dibenzoyl compound is hydrolysed to 5 : 6-diphenyl-2 : 3-dihydro-1 : 2 : 3 : 4-tetrazine, which crystallises in thick needles and melts at 135° (Abstr., 1904, i, 201). It is oxidised to a yellow oil by lead peroxide and sulphuric acid ; when heated with hydrochloric acid at 125°, it forms the hydrochloride ; at higher temperatures, it is decomposed to a viscid, yellow oil, which contains hydrazine. The hydrochloride, $C_{14}H_{12}N_4,HCl$, melts at 183—185°. The benzylidene derivative, $C_{21}H_{16}N_4$, crystallises in matted needles and melts at 184°. When treated with bromine in hot alcoholic solution, diphenyldihydrotetrazine yields α-tolane dibromide, which melts at 205—206°. The action of nitrous acid on diphenyldihydrotetrazine in ethereal solution leads to the formation of 3 : 4-diphenyl-1 : 2 : 5-triazole, which crystallises in slender, white needles and melts at 138° ; the *silver* derivative, $C_{14}H_{10}N_3Ag$, is sensitive to light. G. Y.

A Colourless Hydrochloride of Rosaniline. RUDOLF LAMBRECHT and HUGO WEIL (*Ber.*, 1904, **37**, 4326—4327. Compare Abstr., 1904, i, 877 ; ii, 794).—When rosaniline is crystallised from 2 parts of 30 per cent. hydrochloric acid and the crystals washed with the free acid, a colourless, crystalline *hydrochloride* is obtained. The analyses agree fairly well with the formula $C_{20}H_{21}ON_3,2HCl,4H_2O$. It dissolves in cold water yielding a nearly colourless solution, but when heated yields the ordinary magenta solution. New magenta does not yield crystals under similar conditions. J. J. S.

Phthalonimide and *o*-Phenylenediamine. SIEGMUND GABRIEL (*Ber.*, 1904, **37**, 4316).—On boiling a solution of phthalonimide and *o*-phenylenediamine hydrochloride in water, a compound,

$$C_6H_4\!\left\langle\begin{matrix} N{:}C\text{——}C_6H_4 \\ \quad\quad\quad\quad | \\ N{:}C{\cdot}CO{\cdot}NH \end{matrix}\right.,$$

is obtained, crystallising in yellow needles melting at 267—268°, and

evidently identical with the compound obtained by Manuelli and Silvestri (Abstr., 1904, i, 784) by condensing phthalonic acid with *o*-phenylenediamine and acting on the product with ammonia.

C. H. D.

Desmotropic Compounds. OTTO DIMROTH (*Annalen*, 1904, **335**, 1—112. Compare Abstr., 1903, i, 127).—It is at present believed that there is a relation between the dissociating power of a solvent and its capacity to isomerise desmotropic compounds. In the cases previously studied (Menschutkin, Abstr., 1890, 1366; Stobbe, Abstr., 1903, i, 421), the coefficient of isomerisation increases with the dissociating power of the solvent; the reverse is found to be the case for the isomerisation of methyl 5-hydroxyphenyl-1 : 2 : 3-triazole-4-carboxylate into its keto-desmotrope. The following values for k have been found for the enolic ester: in methyl alcohol solution, at 25°, $k=0·00529$; in ethyl alcohol solution, at 0°, $k=0·000195$, at 18°, 0·00359, at 25°, 0·01017, $k_{25}/k_{15}=4·5$; in acetone, at 25°, $k=0·0527$; in ether, at 18°, $k=0·041$; in chloroform, at 0°, $k=0·00338$, at 18°, 0·0836, at 25°, 0·27, $k_{25}/k_{15}=5·27$; in a saturated aqueous solution, at 25°, $k=0·00023$, at 50°, 0·00126, $k_{50}/k_{40}=4·6$; in aqueous solution, 1·42 grams of enolic ester per 1500 c.c. water, at 50°, $k=0·000663$; 0·71 gram of enolic ester per 1500 c.c. water, at 50°, $k=0·000292$; in saturated aqueous solutions, at 50°, containing 2 mols. of the sodium derivative per mol. of enolic ester, $k=0·00225$, containing 1 mol. of hydrogen chloride per mol. of enolic ester, $k=0·00195$, containing 1·8 mols. of acetic acid per mol. of enolic ester, $k=0·00124$; and saturated in 0·06N sodium chloride solution, at 50°, $k=0·00106$.

As the conversion of methyl 5-hydroxy-1-phenyl-1 : 2 : 3-triazole-4-carboxylate into its keto-modification takes place most rapidly in anhydrous solvents, an additive compound with water cannot form an intermediate stage; neither can the isomerisation be the result of electrolytic dissociation, as k is found to diminish with dilution and to increase on addition of the sodium derivative of the enolic ester (compare Lapworth, Trans., 1902, 81, 1508). The enolic ester can be estimated in presence of the keto-ester by addition of potassium iodide and iodate and titration of the liberated iodine with sodium thiosulphate, as the keto-ester does not take part in the reaction.

The anhydrous enolic ester melts at 74°, resolidifies and again melts at 82°, and gradually changes, at the ordinary temperature, into the keto-ester. It has the molecular conductivity μ_∞ 371 at 25°; 484·5 at 50°. The dissociation constant diminishes with dilution: $V=94·3$, $100K=1·46$; $V=754·4$, $100K=1·09$. The sodium derivative of the enolic ester has the molecular conductivity μ_∞ 75·3 at 25°, 113·5 at 50°.

When dissolved in ether, benzene, or chloroform, the enolic ester undergoes complete isomerisation; in methyl alcohol, a state of equilibrium is reached when the esters are in the proportion 1 of enolic ester : 150 of keto-ester, in ethyl alcohol when the proportion is 1 of enolic ester : 300 keto-ester, and in water 1 of enolic ester : 14 of keto-ester.

The sodium derivative of the enolic ester crystallises in clusters of

needles and loses water of crystallisation at 105°; the *copper* derivative, $C_{20}H_{16}O_6N_6Cu,2H_2O$, forms small, green crystals; the *silver* derivative is obtained as a white precipitate; the *ammonia* derivative is formed immediately by the action of ammonia on the enolic ester in alcoholic or ethereal solution, only slowly by the action of ammonia on the keto-ester in ethereal solution, or incompletely in benzene solution. The *aniline* compound, $C_{10}H_9O_3N_3,C_6H_7N$, formed by the action of aniline on the enolic ester, crystallises in slender needles and melts at 99°; the *phenylhydrazine* compound, $C_{10}H_9O_3N_3,C_6H_8N_2$, is formed by the action of phenylhydrazine on the enolic ester in alcoholic solution, or on fusing the keto-ester with phenylhydrazine at 100°. It crystallises in white needles, melts at 140—141°, and, if heated to 145° and quickly cooled, yields the keto-ester and phenylhydrazine, but if allowed to cool slowly is regained unchanged. A solution of the phenylhydrazine compound, the keto-ester and phenylhydrazine in equilibrium is obtained on boiling the phenylhydrazine compound or the keto-ester and phenylhydrazine in alcohol. The *benzidine* compound, $C_{32}H_{30}O_6N_8$, is formed from benzidine and the enolic ester in alcoholic solution, and melts and decomposes into benzidine and keto-ester at 149°; it is decomposed by dilute sodium carbonate solution or concentrated hydrochloric acid, but not by dilute hydrochloric acid; when boiled with methyl alcohol, it is almost completely decomposed into keto-ester and benzidine. The *dianisidine* compound, $C_{34}H_{34}O_8N_8$, crystallises in small prisms, melts and decomposes at 150°, and is partly decomposed when boiled with methyl alcohol. The *o-tolidine* compound, $C_{34}H_{34}O_6N_8$, formed by the action of *o*-tolidine on the enolic ester, crystallises as a white powder, melts at 145—146°, and is decomposed by aqueous sodium carbonate, but not by dilute hydrochloric acid; when fused or when boiled with alcohol, it yields an isomeric *substance* which is also formed by the action of *o*-tolidine on the keto-ester in alcohol; it crystallises in glistening, yellow needles, melts at 119°, and is decomposed by dilute hydrochloric acid, but not by sodium carbonate solution.

[With E. EBERHARDT.]—The *benzoyl* derivative of the enolic ester, $OBz\cdot C_2N_3Ph\cdot CO_2Me$, formed by the action of benzoic chloride on the sodium compound in ethereal solution, melts at 104—105°. The *ethyl* ether, $OEt\cdot C_2N_3Ph\cdot CO_2Me$, obtained by treating the silver compound with ethyl iodide, crystallises in plates, melts at 93—94°, and is hydrolysed by boiling alcoholic potassium hydroxide to the *acid*,

$$C_{11}H_{11}O_3N_3,H_2O,$$

which, when anhydrous, melts and decomposes at 96—97°. 5-*Ethoxy-1-phenyl*-1 : 2 : 3-*triazole*, formed by heating the carboxylic acid at 100—105°, separates from light petroleum in small crystals and melts at 58—59°.

[With E. LETSCHE.]—5-Hydroxy-1-phenyl-1 : 2 : 3-triazole is best purified by conversion into the colourless *hydrochloride*,

$$C_8H_7ON_3,HCl,$$

which decomposes at 124—125° and yields the hydroxytriazole when treated with water. The *sodium* compound, $C_8H_6ON_3Na$, crystallises in white needles; the *benzoyl* derivative, $C_2N_3HPh\cdot OBz$, formed by the action of benzoic chloride in pyridine solution, crystallises in slender, white needles and melts at 141—142°; with phenylhydrazine or

semicarbazide in alcoholic solution, it forms *s*-benzoylphenylhydrazine and benzoylsemicarbazide respectively, hydroxyphenyltriazole being re-formed.

[With E. EBERHARDT.]—5-Hydroxy-1-phenyltriazole "couples" with diazobenzene chloride in aqueous sodium carbonate solution, forming two substances: a scarlet *compound*, $C_{14}H_{11}ON_5$, which crystallises in needles and melts at 131—132°, and a colourless *compound*,

$$C_{14}H_{11}ON_5,$$

which crystallises in white leaflets and melts at 162—163°.

[With E. LETSCHE.]—When oxidised with potassium permanganate in aqueous sodium carbonate solution, 5-hydroxy-1-phenyl-1 : 2 : 3-triazole yields oxanilic acid, *p*-benzoquinone, and phenyl*iso*nitrile. When boiled with water, 1-phenyl-5-triazolone-4-carboxylic acid yields glycollic anilide and a substance, $C_{17}H_{14}O_4N_4$.

[With E. EBERHARDT.]—When treated with methyl alcohol, 1-phenyl-5-triazolone-4-carboxylic acid yields methoxyacetanilide and a *substance*, $C_{17}H_{14}O_4N_4$, which crystallises in colourless needles, melts at 168°, and with sodium methoxide in methyl alcoholic solution yields glycollic anilide and the sodium salt of hydroxyphenyltriazolecarboxylic acid. When warmed with fuming hydrochloric acid, hydroxyphenyltriazolonecarboxylic acid yields chloroacetanilide.

[With E. LETSCHE.]—5-Benzoxy-1-phenyl-4-methyl-1 : 2 : 3-triazole melts at 91° and is easily hydrolysed by boiling dilute hydrochloric acid, by sodium ethoxide in cold alcoholic solution, and by phenylhydrazine and semicarbazide with formation of *s*-benzoylphenylhydrazine and benzoylsemicarbazide respectively. The action of methyl iodide on the sodium derivative of 5-hydroxy-1-phenyl-4-methyltriazole leads to the formation of a *substance*, $C_{20}H_{23}O_2N_6I$, which melts at 168°, has acid properties, gives a brownish-red coloration with ferric chloride, and yields the hydroxytriazole when warmed with aqueous sodium hydroxide or silver oxide; if an excess of methyl iodide is used for the methylation, a *periodide* which melts at 96° is formed.

The action of phenylhydrazine on 5-hydroxy-1-phenyl-4-methyltriazole leads to the formation of the phenylhydrazone of pyruvic anilide, NHPh·CO·CMe:N·NHPh, which melts at 174°. When boiled with benzene, ether, chloroform, xylene, or toluene, the enolic compound yields a *substance*, $C_9H_8ON_2$, which melts at 163—164° and is stable towards aqueous alkali hydroxides or acids.

5-*Hydroxy*-1 : 4-*diphenyl*-1 : 2 : 3-*triazole*, $NPh<\begin{matrix} N\!=\!=\!=\!N \\ C(OH)\!:\!CPh \end{matrix}$, is obtained in the form of its sodium compound by the action of phenylazoimide on ethyl phenylacetate in presence of sodium ethoxide. The hydroxytriazole, precipitated on addition of hydrochloric acid to the solution of the sodium compound, forms white crystals, melts at 150—151°, is moderately soluble in alcohol, insoluble in water, ether, or benzene, dissolves easily in aqueous alkali hydroxides, and gives no coloration with ferric chloride; the *sodium* compound,

$$C_{14}H_{10}ON_3Na,$$

crystallises in stellate groups; the hydroxytriazole is completely oxidised by potassium permanganate at 40°. The *benzoyl* derivative crystallises in white needles and melts at 132°; the *methyl* ether

crystallises in slender, white needles and melts at 126°. The action of phosphorus pentachloride on 5-hydroxy-1 : 4-diphenyltriazole leads to the formation of 5-*chloro*-1 : 4-*diphenyltriazole*,

$$NPh<\begin{matrix}N{=}N\\ CCl{:}CPh\end{matrix},$$

which crystallises in plates and melts at 137°.

[With E. EBERHARDT.]—The formation of methyl 1-phenyl-5-triazolone-4-carboxylate by the action of phenylazoimide on methyl malonate is accompanied by that of a small amount of a *substance*, $C_7H_8O_5N_2$, which melts at 232°, has acid properties, gives a violet coloration with ferric chloride, when heated at 250—260° evolves carbon dioxide and yields a crystalline product melting at 86—91°, and when heated with fuming hydrochloric acid in a sealed tube forms the hydrochloride of 4-hydroxypyrazole (Wolff, Abstr., 1900, i, 691). It must therefore be methyl 4-hydroxypyrazole-3 : 5-dicarboxylate,

$$NH<\begin{matrix}N{=}{=}{=}{=}C\cdot CO_2Me\\ C(CO_2Me)\cdot C\cdot OH\end{matrix}.$$

G. Y.

2-Aminoadenine (2 : 6-Diaminopurine). WILHELM TRAUBE (*Ber.*, 1904, **37**, 4544—4547. Compare Abstr., 1900, i, 416; 1901, i, 54, 762; 1904, i, 632, 633).—2 : 4 : 6-*Triaminopyrimidine*,

$$NH_2\cdot C<\begin{matrix}N{:}C(NH_2)\\ N\cdot C(NH_2)\end{matrix}>CH,$$

is readily obtained by the condensation of guanidine with malononitrile in alcoholic solution. Its *sulphate*, $C_4H_7N_5,H_2SO_4,H_2O$, is sparingly soluble, and also the *nitrate*, whereas the *hydrochloride* dissolves readily in water. The base crystallises from dilute alcohol in colourless needles. Nitrous acid transforms it into an iso*nitroso*-derivative, which, when reduced with ammonium sulphide, yields 2 : 4 : 5 : 6-*tetraminopyrimidine*. This is best purified by means of its *sulphate*, $C_4H_8N_6,H_2SO_4,3H_2O$. The free base crystallises from water in needles and reduces ammoniacal silver nitrate solution. A *formyl* derivative is obtained by boiling the above sulphate with formic acid and sodic formate; it crystallises in needles, melts at 152—155°, and at the same time loses water, yielding 2-*aminoadenine* (2 : 6-*diaminopurine*), $CH<\begin{matrix}NH\cdot C\cdot C(NH_2){:}N\\ N{-}C\cdot N{=}{=}{=}C\cdot NH_2\end{matrix}$, which crystallises from water in stout prisms. Its solution in nitric acid yields a crystalline precipitate with silver nitrate. It forms well-defined salts with mineral acids, the *nitrate* is very sparingly soluble, and the *platinichloride* crystallises in dark needles relatively readily soluble.

J. J. S.

Azo-derivatives of 3 : 3′-Dihydroxy-2 : 2′-dinaphthyl and 3 : 3′-Dihydroxy-1 : 1′-dinaphthyl. M. EMMANUEL POZZI-ESCOT (*Bull. Soc. chim.*, 1904, [iii], **31**, 1273—1277. Compare Abstr., 1904, i, 789).—3 : 3′-*Dihydroxy*-2 : 2′-*dinaphthyl*-1 : 1′-*disazobenzene*,

$$C_{20}H_{10}(OH)_2(N_2Ph)_2,$$

prepared by the interaction of 3 : 3′-dihydroxy-2 : 2′-dinaphthyl with diazobenzene (2 mols.), is an orange-coloured substance, insoluble in

water, soluble in alcohol with a deep orange colour, and in sulphuric acid with a cherry-red colour. 3 : 3′-*Dihydroxy*-1 : 1′-*dinaphthyl*-4-*azobenzene*, $C_{20}H_{13}O_2 \cdot N_2Ph$, obtained by the interaction of 3 : 3′-dihydroxy-1 : 1′-dinaphthyl with diazobenzene (1 mol.) is red, dissolves in alcohol with an orange colour, in sulphuric acid with a grey colour, and is insoluble in water. 3 : 3′-*Dihydroxy*-1 : 1′-*dinaphthyl*-4 : 4′-*disazobenzene* is dull red, gives a reddish-orange solution in alcohol, a wine-red liquid with sulphuric acid, and is insoluble in water. 3 : 3′-*Dihydroxy*-1 : 1′-*dinaphthyl*-4-*azo*-m-*toluene* is brownish-red, dissolves with this colour in alcohol and sulphuric acid, and is insoluble in water.

3 : 3′-*Dihydroxy*-1 : 1′-*dinaphthyl*-4 : 4′-*disazo*-m-*toluene* is red and gives solutions similar to those of the diazobenzene compound. The *disazo*-p-*nitrobenzene* derivative is bright red, gives a yellowish-orange coloration in alcohol, and greyish-green in sulphuric acid. The *product*, obtained by the interaction of 3 : 3′-dihydroxy-1 : 1′-dinaphthyl with benzidine, is violet, gives a purple solution in alcohol, and bluish-green with sulphuric acid. 3 : 3′-*Dihydroxy*-1 : 1′-*dinaphthyl*-4 : 4′-*disazo*-β-*naphthalene* is red, gives a bright red colour with a mixture of alcohol and xylene, and a blue coloration with sulphuric acid. The azo-dyes obtained from 3 : 3′-dihydroxy-1 : 1′-dinaphthyl are deeper, but less vivid, than those derived from α-naphthol, and, being insoluble, are capable of being printed directly. T. A. H.

Some Diazonium Salts of the Anthraquinone Series. PHILIPP KAČER and ROLAND SCHOLL (*Ber.*, 1904, **37**, 4185—4187).—*Anthraquinone*-1-*diazonium hydrogen sulphate*, $C_{14}H_7O_2 \cdot N_2 \cdot SO_4H$, obtained by diazotising 1-aminoanthraquinone in sulphuric acid solution and precipitating the cooled solution with ether-alcohol, forms bright yellow crystals, which are stable at the ordinary temperature, char on slowly heating, and explode slightly on rapid heating. Anthraquinone is precipitated on warming with acidified alcohol.

1 : 5-*Anthraquinonebisdiazonium hydrogen sulphate*,

$$C_{14}H_6O_2(N_2 \cdot SO_4H)_2,$$

from 1 : 5-diaminoanthraquinone, forms orange crystals, exploding slightly at about 172°.

Anthraquinone-1 : 5-*bisazo*-β-*naphthol* crystallises from nitrobenzene in small, green, metallic rods. The α-*naphthol* derivative crystallises well from phenylhydrazine.

The diazonium sulphates of 1 : 3- and 1 : 8-diaminoanthraquinone are much more readily soluble than the 1 : 5-derivatives. C. H. D.

Sulphur Dyes. PAUL FRIEDLÄNDER and FERD. MAUTHNER (*Zeit. Farb. Text. Ind.*, 1904, 3, 333—337).—The following substances were prepared in order to test the view that the sulphur dyes may contain a disulphide group which, under the action of sodium sulphide, is resolved into the sulphydryl group, thus being rendered soluble.

o-*Chlorothiophenol*, prepared by the reduction of o-chlorobenzenesulphonic chloride, boils at 205—206° and is easily oxidised to form o-*dichlorodiphenyl sulphide*, which crystallises from alcohol in needles and melts at 89—90°; the chlorothiophenol obtained by Otto (*Annalen*,

1868, **143**, 109), which melts at 53—54°, is therefore not the ortho-compound, as usually assumed, but probably the para-derivative.

o-Dihydroxydiphenyl disulphide cannot readily be obtained from the foregoing *o*-chlorothiophenol, but is prepared from diazotised *o*-aminophenol by means of the xanthate reaction; as a by-product in this preparation, the *substance*, $C_6H_4<{}^{S}_{O}>CS$, is formed by the loss of 1EtOH from the xanthate; it crystallises from alcohol in slightly yellow needles melting at 99·5°, and by alcoholic potassium hydroxide is converted quantitatively into thiocatechol, $OH\cdot C_6H_4\cdot SH$.

The *azo*-compound, $S_2[C_6H_3(OH)\cdot N_2\cdot C_{10}H_6\cdot SO_3H]_2$, prepared by coupling *o*-dihydroxydiphenyl disulphide with diazotised naphthionic acid, dissolves in sodium sulphide solution giving a violet-coloured compound (the azo-derivative of the thiophenol), which is reoxidised in the air, regenerating the brownish-orange azo-derivative. A similar change of colour, indicating the formation of a sulphydryl group, occurs in the case of the compound of the same disulphide with diazotised benzidine.

The interaction of *o*-diaminodiphenyl disulphide with hydroquinizarine in presence of boric acid at 100° gives the *dye*,

$$C_6H_4:(CO)_2:C_6H_2<{NH\cdot C_6H_4\cdot S\cdot S\cdot C_6H_4\cdot NH \atop NH\cdot C_6H_4\cdot S\cdot S\cdot C_6H_4\cdot NH}>C_6H_2:(CO)_2:C_6H_4,$$

which crystallises from ethyl benzoate in long, dark blue needles and does not melt at 280°; it is not soluble in sodium sulphide solution.

W. A. D.

Preparation of Crystallised Proteids. Michael Cohn (*Zeit. physiol. Chem.*, 1904, **43**, 41—43).—Crystallised ovalbumin can only be obtained from fresh eggs, otherwise it is obtained in an amorphous condition. The crystals are obtained by the addition of 10 per cent. acetic acid after the removal of globulins by means of ammonium sulphate. A second crop of crystals may be obtained by the further addition of acetic acid.

The best yields of crystallised serumalbumin are also obtained when fresh blood is employed. Some 10—14 c.c. of $N/5$ sulphuric acid are used for each 100 c.c. of liquid, and the crystallisation proceeds more rapidly on a warm than on a cold day. The product is pure only after several recrystallisations by solution in water and precipitation with ammonium sulphate.

The albumin does not become insoluble or amorphous under such treatment.

J. J. S.

Hydrolysis of the Liver Proteid. Julius Wohlgemuth (*Ber.*, 1904, **37**, 4362—4364. Compare Abstr., 1903, ii, 440; 1904, ii, 751). —The nucleoproteid of the liver on hydrolysis with sulphuric acid and subsequent removal of most of the products of hydrolysis by the ester method yielded a residue from which two *copper* salts were obtained. The one, $C_{10}H_{18}O_5N_2Cu$, insoluble in alcohol, yielded an acid, $C_{10}H_{20}O_5N_2$, probably a *diaminohydroxysebacic acid*; the other, $C_8H_{13}O_5NCu$, is soluble in alcohol.

E. F. A.

Deaminoalbumins. S. LEVITES (*Zeit. physiol. Chem.*, 1904, **43**, 202—206).—Deaminoalbumins have been obtained from egg-albumin, casein, and gelatin by Schiff's method (compare Abstr., 1896, i, 632; Paal, *ibid.*, i, 455). The deamino-compounds give both the biuret and Millon reactions, and are less rich in total nitrogen but slightly richer in amino-nitrogen than the substances from which they were obtained. This would indicate that the presence of acid amide, $\cdot CO\cdot NH_2$, groups in the original proteid molecules has not yet been established. J. J. S.

Decomposition of Pseudomucin by Concentrated Boiling Acids. II. J. OTORI (*Zeit. physiol. Chem.*, 1904, **43**, 74—85. Compare Abstr., 1904, i, 1067).—The following products have been obtained by hydrolysing pseudomucin with hydrochloric acid and stannous chloride, according to Hlasiwetz and Habermann's directions (this Journal, 1872, 1069; 1874, 172). The numbers refer to parts per 100 parts of pseudomucin. Ammonia, 3·24; guanidine, 0·025; arginine, 0·777; lysine, 2.58; tyrosine, 0·44; leucine, 4·43; glycine, 0·146; glutamic acid, 0·594; valeric acid, 0·765; acetic (with a little propionic) acid, 0·161; humin, 7·005. Aspartic acid, formic acid, and a reducing sugar are also formed. The differences both as regards the nature and the amount of the products obtained, when sulphuric acid is used on the one hand, and hydrochloric acid and stannous chloride on the other, are accounted for first by the more energetic hydrolytic action of the hydrochloric acid, and secondly by the reducing properties of the stannous chloride.

Small amounts of guanidine have been isolated, in the form of guanidine cadmium chloride, from the products obtained by boiling casein and gelatin with hydrochloric acid.

It is pointed out that ether completely extracts stannous chloride from its aqueous solutions. J. J. S.

Oxidation of Pseudomucin and of Casein with Calcium Permanganate. J. OTORI (*Zeit. physiol. Chem.*, 1904, **43**, 86—92). —Pseudomucin and casein have been oxidised by Zickgraf's method (Abstr., 1903, i, 666; 1904, i, 955), but in neither case did the maximum production of the guanidine (determined as picrate) coincide with the disappearance of the biuret reaction, although on the whole the amount of guanidine showed an increase as the biuret reaction became less marked. The sparingly soluble calcium compounds were worked up according to Kutscher and Schenck's method (Abstr., 1904, i, 955), and a compound subliming at about 260° was obtained from pseudomucin together with a compound melting and decomposing at 330°.

The calcium compound from casein gave oxamic acid or Zickgraf's compound. J. J. S.

Caseinokyrine. MAX SIEGFRIED (*Zeit. physiol. Chem.*, 1904, **43**, 46—67).—*Caseinokyrine* is formed when casein is digested with 12 or 16 per cent. hydrochloric acid at 38—39° during three weeks, and may be isolated by means of phosphotungstic acid and purified by repeated crystallisation of its sulphate in order to free it from small

amounts of tyrosine. Pyrrolidine-2-carboxylic acid is also formed at the same time.

Caseinokyrine sulphate, $C_{23}H_{47}O_8N_9,3H_2SO_4$, has not been obtained in a crystalline form, but the *phosphotungstate* crystallises in much the same manner as glutokyrine phosphotungstate.

Both caseinokyrine and glutokyrine give the biuret reaction. Mercuric sulphate yields a precipitate with caseinokyrine which dissolves on the addition of dilute sulphuric acid, and thus differs from histidine sulphate.

When hydrolysed by heating with 33 per cent. sulphuric acid for 12 hours, the chief products are arginine, lysine, and glutamic acid, but neither histidine nor glycine. The proportions are: basic nitrogen 84—85 per cent., and nitrogen as amino-acids 15—16 per cent. of the total nitrogen. These values agree fairly well with the assumption that caseinokyrine is derived from 1 molecule of arginine, 2 molecules of lysine, and 1 molecule of glutamic acid *minus* 2 molecules of water.

The caseinokyrine was carefully tested and shown to be free from arginine and lysine before hydrolysis. J. J. S.

Glutokyrine. MAX SIEGFRIED (*Zeit. physiol. Chem.*, 1904, **43**, 44—45. Compare Abstr., 1903, i, 587).—Glycine is formed when glutokyrine is boiled with 33 per cent. sulphuric acid for 6 hours. Glutamic acid is also formed. J. J. S.

Preparation and Analysis of Nucleic Acids. VII. PHOEBUS A. LEVENE (*Zeit. physiol. Chem.*, 1904, **43**, 199—201. Compare Abstr., 1901, i, 623; 1903, i, 668, 779; 1904, i, 126, 955).—Lævulic acid has been detected among the products obtained by the hydrolysis with 25 per cent. sulphuric acid at 100° of the nucleic acids from spleen, pancreas, brain, and testicles. The acid was isolated as its silver salt, and not as its phenylhydrazone (compare Inouye, this vol., i, 837). J. J. S.

Cerebrone. HANS THIERFELDER (*Zeit. physiol. Chem.*, 1904, **43**, 21—31. Compare Abstr., 1901, i, 176).—Cerebrone is identical with Gamgee's pseudo-cerebrin (*Text Book of Physiology*, 1880). The name cerebrone is retained. On hydrolysis with 7 per cent. sulphuric acid under pressure, it yields galactose, cerebroic acid, and Thudichum's sphingosine, $C_{17}H_{35}O_2N$.

The formation of galactose is complete after some four hours, and the amount is 20 per cent. of the cerebrone. *Cerebroic acid*, $C_{25}H_{50}O_3$, separates as a snow-white powder from alcohol, melts at 99° when slowly heated, yields a *sodium* salt, $C_{25}H_{49}O_3Na$, and an *acetyl* derivative which has only been obtained in the form of a gelatinous mass. The *sodium* salt of the acetyl derivative, $C_{25}H_{48}O_3AcNa$, has been prepared. J. J. S.

Compounds of Mesoporphyrin with Iron and Manganese. JEAN ZALESKI (*Zeit. physiol. Chem.*, 1904, **43**, 11—17. Compare Abstr., 1903, i, 217, 375).—A solution of mesoporphyrin hydrochloride

in 80 per cent. acetic acid saturated with sodium chloride reacts with ferrous acetate solution yielding a crystalline product which in many respects resembles hæmin. The crystals are darker, thicker, and more pronouncedly triclinic in habit. It does not contain a methoxy-group, and, when heated with acetic acid saturated with hydrogen bromide, it yields mesoporphyrin hydrochloride. The compound does not dissolve in dilute acids or in concentrated hydrochloric acid. Its solutions in chloroform, ether, alcohol, or acetone are more strongly coloured than corresponding solutions of hæmin. It may be repeatedly crystallised from acetic acid without undergoing decomposition, and dissolves readily in dilute alkalis. The absorption spectrum of acetic acid solutions resembles that of hæmin, but the characteristic bands are somewhat nearer the violet end. It yields esters in exactly the same manner as hæmin. The *ethyl* ester forms rhombic crystals insoluble in alkalis, but readily soluble in chloroform, acetone, or ether.

When hæmatoporphyrin is used in place of mesoporphyrin, the product is hæmin, and not the new compound, which probably contains four atoms of hydrogen more in the molecule than hæmin, and it is therefore termed *hydrohæmin*; it has the composition $C_{34}H_{36}O_4N_4ClFe$.

A corresponding *manganese* compound has been obtained by using manganous acetate; it closely resembles the iron compound, but is more readily soluble in acetic acid, and has characteristic absorption band $\lambda 593$—585 and $\lambda 570$—540, and the right end of its spectrum from $\lambda 487$ is quite dark. J. J. S.

Adrenaline and Alkylaminoacetylcatechol. FRIEDRICH STOLZ (*Ber.*, 1904, **37**, 4149—4154. Compare Abstr., 1904, i, 873, 1069, and Jowett, Trans., 1904, **85**, 192).—*Tri-p-chlorobenzoyladrenaline*, $C_9H_{10}O_3N(CO{\cdot}C_6H_4Cl)_3$, forms an uncrystallisable varnish melting at about 75°, and dissolves readily in alcohol, ether, or benzene, but not in water or dilute acids or alkalis.

The author's results obtained by methylating and oxidising adrenaline are identical with those of Jowett (*loc. cit.*). Methyl iodide and methyl-alcoholic sodium hydroxide react with adrenaline to form vanillin. These reactions indicate the formula of adrenaline as being $C_6H_3(OH)_2{\cdot}CH(OH){\cdot}CH_2{\cdot}NHMe$, and it should therefore be possible to synthesise the base by reducing methylaminoacetylcatechol.

[With HANS MEYER (Marburg).]—The alkylaminoacetylcatechols (Abstr., 1904, i, 873) and their reduction products have physiological properties closely resembling those of adrenaline.

Aminoacetylcatechol, $C_8H_9O_3N$, prepared by the action of ammonia on chloroacetylcatechol, forms a yellowish-white, crystalline powder, which darkens at 200° and decomposes slowly at about 300°. The *hydrochloride* crystallises from alcohol in colourless leaflets and melts and decomposes at 260°. C. H. D.

Adrenaline. GABRIEL BERTRAND (*Bull. Soc. chim.*, 1904, [iii], **31**, 1289—1292. Compare Abstr., 1904, i, 956).—Adrenaline crystallises in small lamellæ joined together to form branches which are grouped

into spheres. The prismatic crystals seen in commercial preparations of this material are probably magnesium ammonium phosphate. It is soluble in water to the extent of 0·0268 per cent. at 20°, less than this in alcohol, and not at all in the other common organic solvents, but dissolves in acids and alkalis. A solution in decinormal sulphuric acid had $[\alpha]_D - 53·3°$ (compare Pauly, Abstr., 1904, i, 128, and Jowett, Trans., 1904, **85**, 192). Adrenaline melts on the Maquenne block at 263°. T. A. H.

Action of Amino-acids on Amylase. JEAN EFFRONT (*Bull. Soc. chim.*, 1904, [iii], **31**, 1230—1233. Compare Abstr., 1893, i, 187).—The author finds that the accelerating influence of asparagine on the activity of amylase towards starch is due to the presence of the amino-group and not to that of the amide group, since aspartic acid, glycine, sarcosine, alanine, leucine, and glutamic and hippuric acids exert a similar accelerating action whereas succinamide, acetamide and its homologues, and benzamide exhibit a retarding influence, as do also the amines, hydroxylamine and hydrazine and their salts. This influence of the amino-acids has nothing in common with that due to organic acids, since glycine in presence of acetic acid shows a greater acceleration than the latter. This action would seem to indicate that the amino-acids exert a beneficial influence in the germination of starchy seeds, especially in the initial stages, when but little amylase is present. T. A. H.

Studies on Enzyme Action: Effect of "Poisons" on the Rate of Decomposition of Hydrogen Peroxide by Hæmase. GEORGE SENTER (*Proc. Roy. Soc.*, 1904, **74**, 201—217. Compare Abstr., 1903, ii, 661).—The influence of various substances on the rate of decomposition of hydrogen peroxide by hæmase has been quantitatively studied. Acids markedly retard the decomposition, and their influence is in general proportional to the number of hydrogen ions they contain. Nitric acid, however, is more, and acetic acid is less, "poisonous" than would be expected from the hydrogen ions present. The length of time during which the acid is in contact with the enzyme before the peroxide is added is of no consequence. Further, if the acid is neutralised before the addition of the peroxide, the change takes place at the normal rate. With alkalis also, at least in stronger solutions, there is a retarding effect. The retardation, unlike that due to acids, depends on the period of incubation, but the normal velocity is observed if the alkali has been neutralised previous to the addition of peroxide. The influence of a large number of neutral salts on the rate of decomposition has been studied, without indicating much of a general character. Dilute solutions may have an accelerating influence, concentrated solutions of the same salt a retarding influence. The halogen derivatives of the alkalis and alkaline earths exert a considerable retarding influence, whilst sodium acetate accelerates the decomposition quite appreciably. Substances which have a markedly "poisonous" influence are hydrogen sulphide, hydroxylamine, mercuric chloride and bromide; formaldehyde, mercuric cyanide, carbon monoxide, iodine, and arsenious oxide have a very slight influence on the catalysis.

From the results obtained with acids and alkalis, it is concluded

that at least some enzymes are amphoteric substances. The author favours the view that the poisonous action of the above-mentioned substances is to be referred in most cases to a formation of compounds with the enzyme which are inactive towards hydrogen peroxide.

The solution of hæmase is to be regarded as a two-phase system, and there are therefore reasons for supposing that what is actually measured is the rate of diffusion of the hydrogen peroxide to the enzyme, the rate of actual decomposition of the peroxide by the enzyme being very great (compare Bodenstein, Abstr., 1904, ii, 245; Nernst, Abstr., 1904, ii, 315; Brunner, *ibid.*). J. C. P.

Ferments which Decompose Nuclein Compounds. Alfred Schittenhelm (*Zeit. Physiol. Chem.*, 1904, **43**, 228—239. Compare Abstr., 1904, ii, 752; Jones and Partridge, *ibid.*, 838).—An active enzyme solution has been obtained by precipitating an aqueous extract of spleen with ammonium sulphate, suspending in water with a little chloroform, thoroughly shaking, dialysing, and filtering. Such a solution readily transforms guanine into uric acid when air is passed through the solution, but in the absence of air xanthine is produced. The solution has not the power of hydrolysing nucleic acids to purine bases and then of transforming these into uric acid. The author is of opinion that three distinct ferments take part in the transformation of nucleic acids into uric acid, namely: 1. A *nuclease* which hydrolyses the nucleic acid to purine bases. This enzyme is present in the spleen extract, but not in the solution of the precipitated enzyme. 2. An enzyme *guanase* or *adenase* which has deamidising functions and transforms guanine into xanthine and adenine into hypoxanthine. This enzyme appears to be extremely widely distributed in the animal tissues. 3. An oxidising enzyme, which, in the presence of air, converts hypoxanthine into xanthine and this into uric acid. The last enzyme is not so widely distributed and is localised in certain special organs.

The precipitation of the spleen extract with alcohol yields a product which is not nearly so active as that obtained by precipitating with ammonium sulphate.

Enzymes which are capable of destroying uric acid are also present in spleen and nerve extracts (compare Ascoli, *Pflüger's Archiv*, 1898, **72**, 340). J. J. S.

Saponification of Cocoa Nut Oil by Cytoplasm. Edouard Urbain, L. Saugon, and A. Feige (*Bull. Soc. chim.*, 1904, [iii], **31**, 1194—1198).—Cocoa nut oil is saponified by Nicloux's cytoplasm (Abstr., 1904, ii, 508), but the action is retarded by the fatty acid, and the retarding influence of the free acid is greater the lower its molecular weight. The saponification of the various glycerides in the oil by cytoplasm appears to proceed at the same rate, and Connstein, Hoyer, and Wartenburg's results (Abstr., 1903, ii, 218), which indicate the contrary, were probably due to the retarding influence of the butyric acid liberated in their experiments on the action of cytoplasm on tributyrin. T. A. H.

Organic Chemistry.

Fundamental Conceptions underlying the Chemistry of the Element Carbon. JOHN U. NEF (*J. Amer. Chem. Soc.*, 1904, **26**, 1549—1577).—The fundamental conceptions on which the present system of organic chemistry is based are the constant quadrivalence of carbon and the process of substitution. These conceptions are discussed in the light of recent work, and it is pointed out that they are inadequate, and must be replaced by the conceptions of a variable carbon valency and of dissociation in its broadest sense. The importance of the so-called methylene chemistry is insisted on. It is suggested that at certain temperatures, which vary according to the nature of the groups or atoms united to it, the quadrivalent carbon atom spontaneously becomes bivalent, whilst at lower temperatures the bivalent and quadrivalent carbon atoms are in dynamic equilibrium. The mechanism of substitution must be regarded as the union of an unsaturated molecule with a second molecule to form an additive compound which in many cases subsequently dissociates spontaneously with formation of two new molecules. E. G.

***iso*Hexanes in Roumanian Petroleum.** PETRUS PONI and N. COSTACHESCO (*Ann. Sci. Univ Jassy*, 1904, **3**, 95—102. Compare Abstr., 1903, i, 593).—The nature of the hexanes in the fraction of petroleum from Colibasi distilling between 58° and 66° has been investigated. This fraction was twice refractionated, and the fraction obtained at 61·5—62·5° was treated with nitric acid of sp. gr. 1·4 in a sealed tube at a temperature of 60°.

The nitrated product was dried and fractionated under a pressure of 35 mm. More than half distilled at 75—76°. From the sp. gr. (0·9681 at 0°/0°) and the boiling point (168—170° under 750 mm.), this appears to be γ-nitro-γ-methylpentane.

The fraction of highest boiling point (150—158°) is a dinitro-compound, but it was only obtained in very small quantity. At intermediate temperatures, mixtures of mono- and di-nitro-derivatives were obtained. The hydrocarbon unattacked by the nitric acid is β-methylpentane. The same products were obtained by treating the fractions collected at 59·5—61·5° and 63·5—64·5° in the same manner, and the results indicate that the petroleum fraction examined consists essentially of a mixture of β-methylpentane and γ-methylpentane.

When treated with fuming nitric acid of sp. gr. 1·525, two crystalline products are obtained. One of these is identical with $\beta\gamma\gamma$-trinitro-β-methylpentane. The other forms acicular crystals melting at 85° and appears to be $\beta\beta\gamma$-trinitro-γ-methylpentane (compare Young, Trans., 1898, **73**, 930). Oxalic acid and carbon dioxide were the only oxidation products observed in the action of the nitric acid of sp. gr. 1·4; carbon dioxide alone being formed in the action of the fuming acid. H. M. D.

Preparation of Acetylene Tetrachloride. CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE (D.R.-P. 154657. Compare Berthelot and Jungfleisch, 1870).—Acetylene tetrachloride is best prepared by passing acetylene and chlorine alternately into antimony pentachloride and fractionally distilling the product. The gases may also be passed in simultaneously if precautions are taken to prevent contact between the two gases and to prevent supersaturation at any point.

C. H. D.

Trichloro*iso*propyl Alcohol. EDOUARD VITORIA (*Bull. Acad. Roy. Belg.*, 1904, 1087—1123. Compare Abstr., 1904, i, 279 and 794).—$\gamma\gamma\gamma$-Trichloro*iso*propyl alcohol, $CCl_3\cdot CHMe\cdot OH$, prepared as already described (*loc. cit.*), forms monoclinic crystals similar to those of potassium tetrathionate (the crystallographic measurements are given in the original). It exerts vapour pressures equivalent to 3, 18, and 115 mm. of mercury at 19°, 56°, and 100° respectively. The alcohol could not be deracemised.

$\gamma\gamma\gamma$-*Trichloro*iso*propyl acetate* is a colourless liquid with an odour recalling that of ethyl acetate; it melts at 8°, boils at 180—181° under 766 mm. pressure, has a sp. gr. 1·353 at 15°/15° and n_D 1·46017. The *nitrate* is a colourless or slightly yellow liquid having a sp. gr. 1·499 at 13° and n_D 1·47982. Attempts to prepare the benzoate, chloride, and bromide by the usual methods were unsuccessful.

When treated with phosphoric oxide, trichloro*iso*propyl alcohol furnishes the corresponding $\gamma\gamma\gamma$-*trichloropropylene*, $CCl_3\cdot CH\colon CH_2$, which is a colourless, mobile liquid with an odour like that of aldehyde; it melts at $-30°$, boils at 114—115° under 757 mm. pressure, has a sp. gr. 1·359 at 13°, and readily combines with chlorine to form *pentachloropropane*, $CCl_3\cdot CHCl\cdot CH_2Cl$; this crystallises from warm alcohol in colourless needles, has a camphoraceous odour, and melts at 179—180°. $\gamma\gamma\gamma$-*Trichloro-$\alpha\beta$-dibromopropane*, $CCl_3\cdot CHBr\cdot CH_2Br$, similarly prepared, melts and decomposes slightly at 210°, but in other respects resembles the pentachloropropane.

On oxidation with chromic acid, trichloro*iso*propyl alcohol gave negative results, but with nitric acid some trichloroacetic acid was produced. These results indicate that the alcoholic character of the substance and the reactivity of the H atom in the group $-CH\cdot OH$ are enfeebled by the presence of the three chlorine atoms.

In attempting to prepare various ethers from $\gamma\gamma\gamma$-trichloro*iso*propyl alcohol by the application of the Grignard reaction to tetrachloro-ethers of the type $CCl_3\cdot CHCl\cdot OR$, a series of alkoxydichloropropylenes was obtained. β-*Methoxy-$\alpha\alpha$-dichloropropylene*,

$$CCl_2\colon CMe\cdot OMe,$$

is a colourless liquid, which melts at $-71°$ or $-72°$, boils at 126—127° under 750 mm. pressure, has a sp. gr. 1·239 at 20° and n_D 1·469. β-*Ethoxy-$\alpha\alpha$-dichloropropylene* melts at $-80°$ to $-85°$, boils at 144—146° under 763 mm. pressure, has a sp. gr. 1·179 at 20° and n_D 1·46434. β-*Propoxy-$\alpha\alpha$-dichloropropylene* melts at $-90°$, boils at 163—164° under 764 mm. pressure, has a sp. gr. 1·134 at 20° and n_D 1·45939. All these derivatives readily combine with halogens.

Chloral propyl alcoholate, $CCl_3\cdot CH(OH)\cdot OPr^{\alpha}$, is liquid, and with

phosphorus pentachloride yields the *tetrachloro-ether*, $CCl_3 \cdot CHCl \cdot OPr^a$, which boils at 199—200° under 764 mm. pressure. T. A. H.

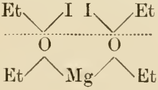
Action of Organomagnesium Compounds on β-Hydroxy-aldehydes and on Keto-alcohols. ADOLF FRANKE and MORITZ KOHN (*Ber.*, 1904, **37**, 4730—4731. Compare Abstr., 1904, i, 845).—A good yield of *pentane-βδ-diol*, $OH \cdot CHMe \cdot CH_2 \cdot CHMe \cdot OH$, may be obtained by the action of magnesium methyl iodide (2 mols.) on aldol; it is a viscid, colourless liquid, distils at 98° under 12 mm. pressure or at 198—199° under 748 mm. The *diacetate* distils at 88° under 10·5 mm., or at 200—202° under the ordinary pressure.

Diacetonealcohol and magnesium methyl iodide yield *βδ-dimethyl-pentane-βδ-diol*, $OH \cdot CMe_2 \cdot CH_2 \cdot CMe_2 \cdot OH$, which is also a viscid liquid with a faint odour of peppermint. It distils at 98° under 13 mm. pressure.

Formyl*iso*butyrylaldol and magnesium ethyl iodide yield, in addition to the hydroxypivalic ester already described (*loc. cit.*), a *glycol*, probably *ββ-dimethylpentane-αγ-diol*, $OH \cdot CH_2 \cdot CMe_2 \cdot CH(OH) \cdot CH_2Me$, which melts at 55° and distils at 211—214°. J. J. S.

Quadrivalent Oxygen. EDMOND E. BLAISE (*Compt. rend.*, 1904, **139**, 1211—1213).—The crystalline compound melting at 52—53°, obtained by the action of magnesium on iodine in the presence of ether, probably has the constitution $OEt_2{<}^{I\ \ I}_{Mg}{>}OEt_2$ (compare Abstr., 1901, i, 317, and Zelinsky, Abstr., 1903, i, 802), and similar compounds are obtained when the ethyl ether in the above reaction is replaced by methyl amyl ether or by phenyl amyl ether, but the products are not crystalline, whilst diethyl methylene ether or ethyl acetate yield the solid compounds $Mg(OEtI \cdot CH_2 \cdot OEt)_2$ and $MgI_2,6MeCO_2Et$ respectively. The basic character of the quadrivalent oxygen in these compounds increases with the complexity of the alkyl groups associated with them; thus, the ethyl ether in the compound of magnesium iodide and ethyl ether is readily replaced by amyl ether, diethyl methylene ether, or by ethyl acetate, and less readily by methyl amyl ether, whilst ethyl ether readily replaces the more acidic phenyl ethyl ether in the compound it forms with magnesium iodide.

Direct evidence in favour of the constitution suggested for the compound of magnesium iodide and ether is afforded by the action of benzoyl chloride at the temperature of boiling water; the products are ethyl iodide, ethyl benzoate, and magnesium chloride, and the following equation represents the reaction:



$+ 2PhCOCl =$ $2EtI + 2PhCO_2Et + MgCl_2$. M. A. W.

Electrolysis of Potassium Acetate. FRITZ FOERSTER and A. PIGUET (*Zeit. Elektrochem.*, 1904, **10**, 924—925).—In reply to the criticisms of Hofer and Moest (this vol., i, 8) of the authors' previous paper on this subject (Abstr., 1904, i, 965), they point out that the fact

that they mistook the nature of the reaction brought about by that portion of the current which does not produce ethane does not affect the accuracy of their determinations of the division of the current between ethane-forming and non-ethane-forming reactions. T. E.

Constitution of Sodium Salts of Certain Acids containing a Methylene or Methinene Grouping. Alkyl Cyanoacetates, Acylcyanoacetates, Malonates, and Cyanomalonates; Malononitrile and Cyanocamphor. ALBIN HALLER and PAUL T. MULLER (*Compt. rend.*, 1904, **139**, 1180—1185. Compare Abstr., 1904, ii, 221).—It has already been shown by one of the authors (Muller, 1902, i, 354; Muller and Bauer, 1903, ii, 705) that the difference between the molecular refraction for the *D* ray of a normal acid and its sodium salt is less than 2 (1·4 to 1·9), whilst the corresponding value in the case of a *pseudo*-acid is greater than 2. In the present paper, the densities and specific refractions for the α, γ, and *D* rays of solutions of approximately equal concentration in absolute alcohol of acids containing a methylene or methinene grouping and their sodium salts are given; the difference between the molecular refraction for the *D* ray of the acid and its salt is in all cases greater than 2, and the following table comprises the results:

	M_D		
Acid.	Salt.	Acid.	Diff.
Ethyl cyanoacetate	33·03	26·84	6·19
Ethyl cyanomalonate	49·48	44·23	5·25
Ethyl cyanopropionylacetate	46·73	44·00	2·73
Ethyl malonate	42·00	38·10	3·90
Malononitrile	21·21	15·67	5·54
Cyanocamphor	54·93	49·18	5·75

Whence it follows that the acids are *pseudo*-acids, that is, the acid and its salts have different chemical constitutions. M. A. W.

Action of Ethyl Sodioacetoacetate on Dibromo-hydrocarbons. ANDREI A. SOLONINA (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 947—988 and 1209—1244).—After discussing the results obtained by other investigators in this direction, the author gives his own results, which are briefly as follows.

With $\alpha\gamma$-dibromobutane, ethyl sodioacetoacetate gives, together with small quantities of acetic and dehydracetic acids, mainly the *ester* $CHMe{<}{\begin{matrix}CH_2-CH_2\\CHAc\cdot CO\end{matrix}}{>}CH\cdot CO_2Et$, which separates in very large prisms, melting at 34° and boiling at 116—118° under 16 mm. pressure; it is readily soluble in alcohol, ether, light petroleum, benzene, or chloroform, and it does not decolorise cold 2 per cent. potassium permanganate solution; sulphuric acid is not coloured by it in the cold, but nitric acid rapidly turns it green; with vanillin and concentrated hydrochloric acid, it gives after some time a red coloration, which is rapidly changed to emerald-green by heating; it gives a liquid compound with phenylhydrazine and only combines with semicarbazide on heating.

Under the action of barium hydroxide, it yields the acid

$$CHMe<\begin{matrix}CH_2\cdot CH_2\\CH_2-CO\end{matrix}>CH\cdot CO_2H,$$

melting at 125—126° (compare Buchner, Abstr., 1898, i, 639); the *silver* salt of this acid was prepared and analysed.

With $\alpha\beta$-dibromo-β-methylpropane, ethyl sodioacetoacetate gives mainly α-bromo-β-methylpropylene and *iso*butylene.

With ψ-butylene bromide (β-butylene bromide), it yields the two stereoisomeric β-bromo-Δ^{β}-butylenes.

With $\beta\delta$-dibromo-β-methylbutane, ethyl sodioacetoacetate yields: (1) a small proportion of ethyl dimethylallyl ether, $CMe_2{:}CH\cdot CH_2\cdot OEt$, but mainly the two following compounds. (2) Ethyl $\delta\delta$-dimethylallylacetoacetate (compare Ipatieff, Abstr., 1901, i, 256), which refractometric and magnetic polarisation measurements show to have the enolic structure, $CMe_2{:}CH\cdot CH_2\cdot C(CO_2Et){:}CMe\cdot OH$. Heating the ester with barium hydroxide solution gives principally the methylheptenone, $CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot COMe$, together with a small quantity of the methylhexenoic acid prepared by Barbier (*Bull. Soc. chim.*, 1887, [ii], **47**, 701) and by Léser (Abstr., 1899, i, 414) and already studied by the author (Abstr., 1902, i, 256). (3) The *ester*

$$COMe\cdot C(CH_2\cdot CH{:}CMe_2)_2\cdot CO_2Et,$$

which boils at 140—149° under 13 mm. pressure and at 280—290° under the ordinary pressure; on heating with barium hydroxide solution, it gives the *ketone* $COMe\cdot CH(CH_2\cdot CH{:}CMe_2)_2$, which boils at 230°, and the *acid* $CH(CH_2\cdot CH{:}CMe_2)_2\cdot CO_2H$, boiling at 121—131° under 13 mm. pressure, the *silver* salt of which was prepared.

With $\beta\gamma$-dibromo-β-methylbutane, ethyl sodioacetoacetate gives principally α-bromo-α-methyl-Δ^{β}-butylene.

With $\beta\delta$-dibromopentane, ethyl sodioacetoacetate yields mainly the *ester* $CMe_2{:}CH\cdot CHMe\cdot CHAc\cdot CO_2Et$, which boils at 120—125° under 18 mm. pressure and at 234—238° under ordinary pressure, and has the sp. gr. 0·99395 at 0°/0° and 0·97712 at 19°/0°; the enolic formula is indicated by refractometric and magnetic rotation measurements. When boiled with barium hydroxide solution, it undergoes principally the ketonic decomposition, yielding the *ketone*

$$CMe_2{:}CH\cdot CHMe\cdot CH_2\cdot COMe,$$

which boils at 178—189°, has the sp. gr. 0·87030 at 0°/0° and 0·85404 at 19·4°/0°, and forms a *semicarbazone*, $C_{10}H_{19}ON_3$, melting at 140°; the ketone is accompanied by a small quantity of the acid $CMe_2{:}CH\cdot CHMe\cdot CH_2\cdot CO_2H$, the silver salt of which was prepared and analysed.

With $\beta\epsilon$-dibromohexane, ethyl sodioacetoacetate gives (1) the *ester* $\begin{matrix}CH_2\cdot CHMe\\|\\CH_2\cdot CHMe\end{matrix}>CAc\cdot CO_2Et$, which boils at 125—130° and has the sp. gr. 1·0617 at 0°/0° and 1·0457 at 19·2°/0°; (2) the *ester* $C_2H_4(CHMe\cdot CHAc\cdot CO_2Et)_2$, boiling at 120—125°.

With $\alpha\gamma$-dibromo-γ-ethylpentane, ethyl sodioacetoacetate yields mainly the unsaturated *ester*, $CEt_2{:}CH\cdot CH_2\cdot CHAc\cdot CO_2Et$, which boils at 142—147° under 14 mm. pressure and has the sp. gr. 0·9854 at 0°/0° and 0·9713 at 16·8°/0°. When heated with barium hydroxide, the ester gives mainly ketone with a small proportion of acid.

With *p*-xylylene dibromide, ethyl sodioacetoacetate gives exclusively the *ester* $C_6H_4(CH_2\cdot CHAc\cdot CO_2Et)_2$, which is deposited from alcohol in crystals melting at 62·5°. When heated with barium hydroxide or dilute potassium hydroxide solution, this yields: (1) the *compound* $C_6H_4(CH_2\cdot CH_2Ac)_2$, which crystallises from alcohol in shining plates melting at 53—54° and is readily soluble in benzene or ether; (2) the *acid* $CH_2Ac\cdot CH_2\cdot C_6H_4\cdot CH_2\cdot CHAc\cdot CO_2H$, separating from water in crystals melting at 206°; the *silver* salt was prepared and analysed; (3) small quantities of acetic, dehydracetic, and an unknown acid.

With *o*-xylylene dibromide, ethyl sodioacetoacetate gives: (1) the *ester* $C_6H_4{<}{\substack{CH_2\\CH_2}}{>}CAc\cdot CO_2Et$, which boils at 185—190° under 21 mm. pressure and has the sp. gr. 1·122666 at 0°/0° and 1·106205 at 19·2°/0°, and n_D 1·51144 at 19·2°. When heated with barium hydroxide solution, it yields (*a*) the *compound*, $C_6H_4{:}(CH_2)_2{:}CHAc$, which boils at 164—168° under 47 mm. pressure, has the sp. gr. 1·0685 at 0°/0° and 1·0546 at 17·5°/0°, and n_D 1·53320 at 22°; the *semicarbazone*, $C_{12}H_{15}ON_3$, of this methyl hydrindeneketone separates from alcohol in white, silky needles melting at about 178°; (*b*) *o* hydrindonaphthenecarboxylic acid (Perkin and Révay, Trans., 1894, **65**, 228); (2) the *ester*, $C_6H_4(CH_2\cdot CHAc\cdot CO_2Et)_2$, which boils at 222—256° under 20—23 mm. pressure.

With *m*-xylylene dibromide, ethyl sodioacetoacetate yields the *ester*, $C_6H_4(CH_2\cdot CHAc\cdot CO_2Et)_2$, which boils at 251—255° under 58—60 mm. pressure, has the sp. gr. 1·107871 at 0°/0° and 1·09385 at 16·8°/0°, and n_D 1·495256 at 19·7°.

With semicarbazide, it gives the *semicarbazone*,

$$\begin{matrix}NH\cdot CO\\ \vert\\ N{:}CMe\end{matrix}{>}CH\cdot CH_2\cdot C_6H_4\cdot CH_2\cdot CHAc\cdot CO_2Et,$$

which separates from water in crystals melting and decomposing at 230°, and is soluble in ethyl or amyl alcohol, ether, ethyl acetate, or *m*-xylene. When heated with barium hydroxide solution, the ester yields: (1) the *ketone*, $C_6H_4(CH_2\cdot CHAc)_2$, melting at 202—207° under 23 mm. pressure and giving a *semicarbazone*, $C_{16}H_{24}O_2N_6$, melting and decomposing at 184°; (2) *m*-phenylenedipropionic acid.

Concerning the action of ethyl sodioacetoacetate on dibromo-derivatives of hydrocarbons, the following conclusions are drawn: (1) if the atoms of bromide in a dibromide with an open chain are not attached to neighbouring carbon atoms, products of combination of ethyl acetoacetate are always formed; if one bromine atom is tertiary and the other primary or secondary, unsaturated compounds with one or two double linkings are obtained; in the absence of a tertiary bromine atom, unsaturated acetoacetic esters are not formed, but esters of keto-acids with a polymethylene ring or else diacetoacetic esters; finally, condensation may occur and give rise to esters of keto-acids with a keto-polymethylene ring. (2) If the two atoms of bromine in a dibromide having an open chain are attached to two neighbouring carbon atoms, the compound does not combine with ethyl acetoacetate unless it contains one primary bromine atom. (3) When the bromine atoms are situated in a benzene or anthracene ring, no combination takes place with ethyl acetoacetate. (4) When

the bromine atoms are in side-chains of aromatic compounds, the reaction proceeds just as with aliphatic dibromo-compounds, and if the bromine atoms are in side-chains having the *o*-position to one another, the ring is simply closed, whilst where the side-chains are in the meta- or para-positions products are always obtained containing two aceto-acetic residues. (6) All the products of combination of ethyl aceto-acetate, obtained by the action of ethyl sodioacetoacetate on di-bromides, may be ranged in the three following classes: (I) esters of β-keto-acids containing a polymethylene ring, formed by the replacement of two atoms of bromine by an ethyl acetoacetate residue, such as

$$\begin{matrix} CH_2\cdot CHMe \\ | \\ CH_2\cdot CHMe \end{matrix}\!\!>\!CAc\cdot CO_2Et.$$

(II) Unsaturated esters of β-keto-acids, divisible into two groups: (*a*) those containing one double bond in the radicle, formed after the action of ethyl sodioacetoacetate, for instance,

$$CMe_2\colon CH\cdot CHMe\cdot CHAc\cdot CO_2Et\,;$$

(*b*) those containing two double bonds in the radicle, formed after the action of ethyl sodioacetoacetate, for instance,

$$COMe\cdot C(CH_2\cdot CH\colon CMe_2)_2\cdot CO_2Et.$$

(III) Esters of keto-acids containing two ethyl acetoacetate residues and divisible into two classes: (*a*) diacetoacetic esters, such as $C_6H_4(CH_2\cdot CHAc\cdot CO_2Et)_2$; (*b*) keto-polymethylene esters of keto-acids, such as $\begin{matrix} CHMe\cdot CH_2\cdot CH_2 \\ | \qquad\qquad\quad | \\ CHAc\cdot CO\text{—}CH\cdot CO_2Et \end{matrix}$.

T. H. P.

The Reduction of the Anhydrides of Dibasic Acids. GUSTAVE BLANC (*Compt. rend.*, 1904, **139**, 1213—1214).—When the anhydride of an unsymmetrical dibasic acid of the type $CH_2\!<\!\begin{matrix} CRR'\cdot CO \\ CH_2\text{—}CO \end{matrix}\!>\!O$ was reduced by sodium and absolute alcohol (compare Bouveault and Blanc, Abstr., 1903, i, 597, 673, 730; 1904, i, 213), a yield of 20—50 per cent. of the lactone, $CH_2\!<\!\begin{matrix} CRR'\cdot CO \\ CH_2\cdot CH_2 \end{matrix}\!>\!O$, was obtained, and normal results were obtained with the anhydrides of pyrotartaric, $\alpha\alpha$-dimethylsuccinic, $\alpha\alpha$-dimethylglutaric, $\beta\beta$-dimethylglutaric, and camphoric acids. *iso*-Propylsuccinic anhydride yielded a lactone which, on treatment with potassium cyanide and subsequent hydrolysis, gave a mixture of α- and β-*iso*propylglutaric acids, in which the latter preponderated.

M. A. W.

Solubility of Metallic Succinates in Water. H. CANTONI and D. DIOTALEVI (*Bull. Soc. chim.*, 1905, [iii], **33**, 27—36).—The solubilities of barium, strontium, calcium, copper and lead succinates in water at temperatures ranging from 0—50° have been determined, and in the cases of the alkaline earth metals compared with those of the malonates and oxalates. The results, which are given in tabular form in the original, show that the solubility of barium succinate slowly increases between 0° and 20° and then diminishes; that of strontium increases from 0—30°, then diminishes between 30° and 40°, and beyond this temperature again increases. Those of the calcium and lead salts increase

steadily with rise of temperature, whilst that of copper succinate increases until the temperature reaches 39° and then diminishes. It is suggested that the alternating changes in the case of the strontium salt are due to changes in the state of hydration and in that of the barium salt to polymorphism.

At 20°, the solubility of the three alkaline earth succinates decreases in the order strontium, barium, calcium, and at 40° in the order barium, strontium, calcium. T. A. H.

Modes of Formation and Preparation of Aliphatic Aldehydes and a General Synthetical Method for the Preparation of Aldehydes. Louis Bouveault (*Bull. Soc. chim.*, 1904, [iii], **31**, 1306—1322, 1322—1327).—The first paper is a *résumé* of methods which have been devised from time to time for the preparation of aldehydes. The second paper deals in greater detail with the process already described by the author (Abstr., 1904, i, 13), which consists in gradually adding disubstituted formamides dissolved in dry ether to magnesium alkyl haloids (compare Beis, Abstr., 1904, i, 15, and Bodroux, *ibid.*, i, 421). The best yields are obtained when diethylformamide is employed. In addition to the aldehydes, other secondary products are formed in the reaction, in particular paraffins, produced by combination of two alkyl groups of the magnesium alkyl haloid employed. When dimethylformamide reacts with magnesium *iso*amyl chloride, there is formed as a by-product *dimethylaminodiamylmethane* [*ζ-dimethylaminoundecane*], $CH(C_5H_{11})_2 \cdot NMe_2$, a liquid having a characteristic amine-like odour and boiling at 110° under 15 mm. pressure and giving a *picrate* which is crystalline and melts at 103°.

The primary and secondary alkyl haloids react normally both in the Grignard reaction and in the subsequent interaction with formamides, but the magnesium derivatives of the tertiary haloids behave differently. The base formed together with amylene by the interaction of magnesium *tert.*-amyl chloride and diethylformamide (Abstr., 1904, i, 546) is probably produced in the manner indicated by the following scheme: $2CMe_2Et \cdot MgCl + H \cdot CO \cdot NEt_2 = MgO + MgCl_2 + NEt_2 \cdot CH(CMe_2Et)_2 = CMe_2Et \cdot CH_2 \cdot NEt_2 + CMe_2\!:\!CHMe$. A number of aldehydes prepared by this process are referred to in the original.

T. A. H.

General Method of Synthesising Aldehydes by means of the Substituted Glycidic Acids. Georges Darzens (*Compt. rend.*, 1904, **139**, 1214—1217).—The ethyl esters of the disubstituted glycidic acids, readily prepared by the condensation of the corresponding ketone and ethyl chloroacetate in the presence of sodium ethoxide according to the equation $CORR' + CH_2Cl \cdot CO_2Et = O{<}\begin{matrix} CRR' \\ | \\ CH \cdot CO_2Et \end{matrix} +$ HCl, are colourless, odourless liquids boiling 60—70° higher than the corresponding ketones and not reacting with bromine, hydroxylamine, phenylhydrazine, or phenylurethane. The disubstituted glycidic acids obtained by hydrolysing the esters are unstable and readily break down into carbon dioxide and the corresponding aldehyde according to the equation $O{<}\begin{matrix} CRR' \\ | \\ CH \cdot CO_2H \end{matrix} =$

CHRR′·COH + CO_2. The boiling points of the ethyl disubstituted glycidates and the aldehydes thus prepared and the melting points of the semicarbazide of the latter are given in the following table:

Ketone.	Boiling point of corresponding ethyl glycidate.	pressure.	Boiling point of aldehyde.	pressure.	Melting point of semicarbazide.
Acetone	163–168°	under 760 mm.	—		—
Methyl *iso*hexyl ketone	151–152	,, 30 ,,	90°	under 40 mm.	60°
Methyl heptyl ketone	155–156	,, 19 ,,	105–106	,, 20 ,,	66–67
Methyl nonyl ketone	165–170	,, 16 ,,	119–122	,, 16 ,,	85
Acetophenone	153–159	,, 20 ,,	95–97	,, 19 ,,	153–154
Tolyl methyl ketone	160–164	,, 16 ,,	107–108	,, 19 ,,	159–160
p-Ethyl acetophenone	210–215	,, 19 ,,	118–120	,, 20 ,,	—
Benzylacetone	175–180	,, 16 ,,	129–130	,, 19 ,,	70–72
Phenyl propyl ketone	155–158	,, 18 ,,	122–123	,, 28 ,,	115–116
*iso*Butylacetophenone	175–180	,, 16 ,,	153	,, 30 ,,	185–186
Methyl*cyclo*hexanone	131–132	,, 15 ,,	66–67	,, 16 ,,	138–139

M. A. W.

Chloromalonaldehyde [β-Chloro-Δ^{β}-propene-γ-ol-α-al]. WALTER DIECKMANN and LUDWIG PLATZ (*Ber.*, 1904, **37**, 4638—4646)—*β-Chloro-γ-anilino-α-phenylimino-Δ^{β}-propylene hydrochloride*,

NHPh·CH:CCl·CH:NPh,HCl,

obtained by heating mucochloric acid (Simonis, Abstr., 1901, i, 268) with alcoholic aniline, crystallises from alcohol with 1EtOH in golden-yellow needles, and melts and decomposes at 228°; on adding it to an excess of boiling water, *β-chloro-γ-anilino-Δ^{β}-propene-α-al* (*monoanilide* of *chloromalonaldehyde*), NHPh·CH:CCl·CHO, is obtained in long, nearly colourless needles; it melts and decomposes at 193° and is hydrolysed by 30 per cent. aqueous potassium hydroxide giving *chloromalonaldehyde*, OH·CH:CCl·CHO, which crystallises from chloroform in slender, colourless needles, melts and decomposes at 144°, readily reduces Fehling's solution, and gives, on dissolution in the aqueous alkali hydroxides, crystalline *sodium* and *potassium* derivatives. Aniline converts the aldehyde into the mono- and di-anilides just described, and with phenylhydrazine 4-*chloro*-1-*phenylpyrazole*,

$$NPh{<}\begin{matrix}CH{:}CCl\\ \quad\ \ |\\ N{=}CH\end{matrix},$$

is obtained; it crystallises from dilute alcohol in colourless needles and melts at 75°. *β-Chloro-γ-methylanilino-Δ^{β}-propene-α-al*,

NMePh·CH:CCl·CHO,

prepared by the action of methylaniline on chloromalonaldehyde in alcoholic solution, forms colourless crystals and melts at 76°. The *benzoate*, CHO·CCl:CH·OBz, of chloromalonaldehyde forms colourless needles and melts at 105°.

β-Bromo-γ-anilino-α-phenylimino-Δ^{β}-propylene hydrobromide,

NHPh·CH:CBr·CH:NPh,HBr,EtOH,

obtained from mucobromic acid and aniline, crystallises from alcohol in golden needles and melts and decomposes at 217°. *β-Bromo-γ-anilino-Δ^{β}-propene-α-al* crystallises from alcohol in colourless needles

melts and decomposes at 184°, and is easily convertible into bromomalonaldehyde, which has already been described by Lespieau (Abstr., 1902, i, 13). 4-*Bromo*-1-*phenylpyrazole* crystallises from alcohol in colourless needles and melts and decomposes at 81°.

Incidentally the following substances are described. *Sodium* *αβ-dibromo-ε-phenyl-$\Delta^{\alpha\gamma}$-pentadiene-ε-one-α-carboxylate*,

$$COPh\cdot CH\colon CH\cdot CBr\colon CBr\cdot CO_2Na,$$

obtained by the condensation of acetophenone and mucobromic acid, forms colourless crystals and decomposes at 154°. The lactone, $\begin{matrix} CBr\cdot CH\cdot CH_2Bz \\ \Vert \quad > O \\ CBr\cdot CO \end{matrix}$, of *αβ-dibromo-ε-phenyl-Δ^{α}-pentene-γ-ol-ε-one-α-carboxylic acid* crystallises from alcohol in colourless leaflets and melts at 168°. The analogous *lactone*, $\begin{matrix} CCl\cdot CH\cdot CH_2Bz \\ \Vert \quad > O \\ CCl\cdot CO \end{matrix}$, is similar and melts at 121—122°. W. A. D.

Migration of the Ethylenic Linking in Alkyl Allyl Ketones. EDMOND E. BLAISE (*Bull. Soc. chim.*, 1905, [iii], **33**, 43—49. Compare Abstr., 1904, i, 290).—When alkyl allyl ketones are treated with hydrogen bromide even at $-80°$, they are converted into saturated bromo-ketones which, on treatment with potassium hydrogen carbonate, furnish alkyl propenyl ketones isomeric with the original alkyl allyl ketones, indicating that in these circumstances the ethylenic linking migrates from the αβ- to the βγ-position.

A similar change is brought about directly by boiling the ketones with dilute sulphuric acid (20 per cent.); the yield of the isomeride in this case is from 60—70 per cent., the loss being due partly to hydration of the ketone and partly to polymerisation. With sodium ethoxide, the alkyl allyl ketones furnish the corresponding ethoxyketones, thus ethyl allyl ketone under these conditions yields ethyl β-ethoxypropyl ketone. Further, when propyl allyl ketone (2 mols.) is boiled with formaldehyde (1 mol.) in presence of piperidine, no condensation occurs, but propyl propenyl ketone is formed.

The bromides of the alkyl allyl ketones are readily distinguished from their isomerides by ebullition with an aqueous solution of an alkali carbonate, the former yielding a colourless distillate, whereas the latter furnish α-diketones which are yellowish-green, thus:

$$R\cdot CO\cdot CHBr\cdot CHBrMe \longrightarrow R\cdot CO\cdot CBr\colon CHMe \longrightarrow R\cdot CO\cdot C(OH)\colon CHMe \longrightarrow R\cdot CO\cdot COEt.$$

The interaction with semicarbazide also serves to distinguish these two classes of unsaturated ketones, the alkyl allyl ketones furnishing under all conditions semicarbazones, whereas their isomerides furnish, with 1 mol. of semicarbazide, semicarbazones, and with 2 mols. of the reagent, semicarbazide-semicarbazones; the propenyl ketones also behave in the same way with hydroxylamine. The *semicarbazones* of methyl-, ethyl-, and propyl-propenyl ketones melt at 114°, 157°, and 147° respectively. A specimen of *ethyl semicarbazopropyl ketone semicarbazone*, $CHMe(NH\cdot CO\cdot NH\cdot NH_2)\cdot CH_2\cdot CEt\colon N\cdot NH\cdot CO\cdot NH_2$, which could not be obtained pure, melted at 157°. The hydroxylamino-

oxime derived from the same ketone is liquid, as is also its benzoyl derivative (compare Rupe and Schlochoff, Abstr., 1904, i, 144).

T. A. H.

Constitution of Cellulose. CHARLES F. CROSS and EDWARD J. BEVAN (*Zeit. Farb. Text. Ind.*, 1904, **3**, 441—442).—A reply to Green (this vol., i, 22).

W. A. D.

Humic Acid. PH. MALKOMESIUS and ROBERT ALBERT (*J. pr. Chem.*, 1904, [ii], **70**, 509—515).—Cassell brown, sold as an artist's colour, contains 90 per cent. of humus substances, from which humic acid, containing only 0·87 per cent. of ash, is obtained by extraction with lithium carbonate and water and addition of hydrochloric acid to the filtrate. Humic acid so obtained gives C = 60·03, H = 4·40, N = 1·09 per cent.; when treated with concentrated nitric acid, it forms a reddish-brown *nitro*-derivative, which has the composition C = 55·52, H = 4·51, N = 3·80, S = 0·92, ash = 0·82 per cent., is easily soluble in methyl or ethyl alcohol, glacial acetic acid, or acetone, and, when heated with bromine or glacial acetic acid in a sealed tube at 100°, yields a *bromo*-derivative containing 41—43 per cent. of bromine.

G. Y.

Aminoethyl Ether. LOUIS HENRY (*Bull. Acad. Roy. Belg.*, 1904, 984—994. Compare Knorr, Abstr., 1904, i, 854).—The author has shown (Abstr., 1901, i, 16) that in two carbon compounds the substitution of the OH group by NH_2 leads to an abnormal rise in boiling point when an amino-alcohol is the product of the reaction, and has ascribed this to the mutual influence of the OH and NH_2 groups. He now points out that the substitution of an OEt group by NH_2 in such cases with the formation of an amino-ether gives rise to a normal increase in boiling point, affording evidence of the validity of his explanation. Thus the difference between the boiling points of ethyl ether and ethylamine is 16°, and that between those of the diethyl ether of glycol and aminoethyl ether is 14° or 15°. Further evidence of the mutual influence of the OH and NH_2 groups in the amino-alcohols is afforded by a comparison of their densities in the liquid state with those of the corresponding alcohols and amines.

The substitution of OH by OEt in compounds of the type $XCH_2·CH_2·OH$ leads to a fall in the boiling point, and the amount of this depends on both the mass and the nature of the group X. These statements are illustrated by examples in the original.

T. A. H.

Synthesis of Serin and Cystin. EMIL ERLENMEYER, jun., and F. STOOP (*Annalen*, 1904, **337**, 236—263. Compare Abstr., 1903, i, 29, 791).—The synthesis of serin (α-amino-β-hydroxypropionic acid) has been achieved by a method differing materially from that of Fischer and Leuchs (Abstr., 1903, i, 12).

Ethyl hippurate condenses with ethyl formate forming the oxy-

methylene compound, $OH\cdot CH:C(NHBz)\cdot CO_2Et$, which, on reduction, gives the ester of benzoylserin, $OH\cdot CH_2\cdot CH(NHBz)\cdot CO_2Et$; the latter can be hydrolysed either to benzoylserin or to serin.

Ethyl hippurate is best prepared by passing hydrogen chloride into a boiling solution of hippuric acid in alcohol and crystallising the product from benzene or ether. When treated with sodium ethoxide, the ester yields a *sodium* derivative, $ONa\cdot CPh:N\cdot CH_2\cdot CO_2Et$, as a white, crystalline precipitate. *Ethyl formylhippurate* was prepared by adding ethyl formate to a solution of sodium ethoxide, when the sodium derivative separates; unless both the alcohol and the sodium are quite pure, decomposition takes place with the evolution of carbon monoxide. Ethyl hippurate is now added, when the mixture sets to a crystalline mass and is kept for ten days, when the *sodium* derivative,

$$C_{12}H_{12}O_4NNa,$$

is collected; the *ester* is difficult to obtain from the sodium derivative in a solid state, but when pure crystallises in needles melting at 128°. The *ethyl* ester of *benzoylserin* is prepared by reducing the ethyl formylhippurate with aluminium amalgam in moist ether, and crystallises from benzene in needles melting at 80°. *Benzoylserin*,

$$OH\cdot CH_2\cdot CH(NHBz)\cdot CO_2H,$$

is prepared by hydrolysis of the ester by alcoholic sodium hydroxide, and forms crystals melting at 159°. The ester of benzoylserin can be converted into serin by prolonged boiling with sulphuric acid (1 in 15), the use of sulphuric acid of any other strength either not effecting the hydrolysis or causing decomposition; the serin was characterised by conversion into its copper salt, and by measurement of the crystals.

Baumann's formula for cystein, $SH\cdot CMe(NH_2)\cdot CO_2H$, which was long accepted as correct, represents this substance as a derivative of thiopyruvic acid. There is no strong evidence, however, in favour of this formula: the known facts rather support one of the expressions $SH\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$ or $NH_2\cdot CH_2\cdot CH(SH)\cdot CO_2H$; since the former represents it as a thioserin, it is the more probable. The work of Neuberg (Abstr., 1902, i, 743) and Friedmann (Abstr., 1902, i, 731; 1903, i, 75, 301) has shown this view to be correct. The synthesis of serin, therefore, rendered possible a synthesis of cystine, and it was found that the oxygen of the hydroxy-group in the ethyl ester of benzoylserin could be replaced by sulphur by the action of phosphorus pentasulphide, the ethyl ester of benzoylcystein,

$$SH\cdot CH_2\cdot CH(NHBz)\cdot CO_2Et,$$

being produced. The ester is molten with twice the theoretical quantity of phosphorus pentasulphide, being heated finally for 8 hours at 120°; the product is extracted with alcohol and recrystallised from ether; it forms colourless needles melting at 158°. On boiling the ester with hydrochloric acid, it is hydrolysed to cystein, which was recognised by means of the additive compound with mercuric chloride. Cystein is very readily oxidised to cystin, the process being best carried out by drawing air through the warmed solution in ammonia. The cystin thus obtained was identical in all respects with the natural cystin prepared from urine with the exception that it was inactive towards polarised light. K. J. P. O.

Polypeptides of the Diamino-acids. Emil Fischer and Umetaro Suzuki (*Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 1333—1341. Compare Abstr., 1903, i, 645, 799, 800; 1904, i, 771; this vol., i, 30).—The diamino-acids, so important biologically, are converted, on heating their methyl esters, into dipeptide and diketopiperazine derivatives.

Methyl diaminopropionate hydrochloride, $C_4H_{10}O_2N_2,2HCl$, conveniently prepared by the action of dry methyl alcohol and hydrogen chloride on the hydrochloride of diaminopropionic acid, melts and decomposes at 166° (corr.); the free *ester* is obtained from this by the action of sodium and methyl alcohol as a colourless, strongly alkaline syrup.

Methyl diaminopropionate dipeptide,

$$NH_2\cdot CH_2\cdot CH(NH_2)\cdot CO\cdot NH\cdot CH_2\cdot CH(NH_2)\cdot CO_2Me\ (?),$$

is prepared by heating the foregoing ester at 100° for an hour, and purified by conversion into the picrate or hydrochloride. The *picrate* forms yellow crystals sparingly soluble in water, which, on heating, darken at 170—180° and melt and decompose between 200° and 210°; the *hydrochloride* is an almost colourless, dense powder sintering at 90° and decomposing at 135°.

Methyl lysine hydrochloride, prepared by the action of methyl alcohol and hydrogen chloride on *r*-lysine hydrochloride, crystallises in colourless, oblique prisms, melting and decomposing at 218°. *Lysine anhydride* is obtained on heating methyl lysine at 100°, as a slightly brown, limpid mass; the *picrate*, $C_{12}H_{24}O_2N_4,2C_6H_3O_7N_3$, crystallises from water in small, yellow prisms or plates which, when heated, darken at 210° and melt and decompose at 230° (corr.); the *hydrochloride* forms microscopic, colourless needles melting and decomposing at 270° (corr.).

Histidine anhydride, $C_{12}H_{14}O_2N_6$, prepared from the methyl histidine hydrochloride described by Pauly (Abstr., 1904, i, 1068), crystallises in colourless, glistening prisms, darkening about 260° and melting to a brown liquid at about 340°.

Methyl arginine hydrochloride, prepared from the double salt of arginine and copper nitrate, crystallises in long, colourless needles or prisms melting and decomposing at 195° (corr.). E. F. A.

Action of Potassium Thiocyanate on Metallic Oxides at High Temperatures. Jar. Milbauer (*Zeit. anorg. Chem.*, 1904, 42, 433—449).—Potassium thiocyanate melts at 171—172°, becomes brown at 300°, and assumes a blue tint at 405°. It was heated with various metallic oxides in vessels of porcelain or of glass, and at temperatures ranging from 200° to 1200°. At 300°, lead monoxide reacts with potassium thiocyanate according to the equation $PbO + KCNS = PbS + KCNO$. The action of zinc oxide and of cadmium oxide is similar. The action with stannic oxide proceeds in two stages, namely: (1) $2KSCN + SnO_2 = SnS + K_2S + 2CO + N_2$ and (2) $KCNS + K_2S + SnS = K_2SnS_3 + KCN$, the latter action proceeding at a temperature higher than that at which the first action takes place. When manganous oxide was used, manganese sulphide was generally produced; in one case, manganese potassium sulphide was isolated. With cupric oxide, cuprous sulphide was produced, whilst

the double sulphide $K_2Cu_8S_6$ was formed at more elevated temperatures, thus: $2CuO + 2KSCN = Cu_2S + K_2S + 2CO + N_2$ and $4Cu_2S + K_2S + KSCN = K_2Cu_8S_6 + KCN$. With molybdenum oxide, the sulphides MoS_2 and MoS_3 were isolated. Bismuth oxide yielded bismuth sulphide, mixed with the double sulphide $Bi_2K_2S_4$ when higher temperatures were employed. Chromium oxide yielded the *compound* $K_2Cr_2S_4$, which forms glistening, metallic, greenish-grey crystals, insoluble in warm hydrochloric acid, and which at a red heat decompose to form sulphur dioxide and chromium oxide. Its formation is represented by the equations: (1) $Cr_2O_3 + 3KSCN = Cr_2S_3 + 3KCNO$, (2) $2KCNO + KSCN = K_2S + KCN + 2CO + N_2$, (3) $Cr_2S_3 + K_2S = K_2Cr_2S_4$. With ferric oxide at 400°, the sulphide $K_2Fe_2S_4$ was produced. Cobalt oxide formed the sulphide $K_2Co_{11}S_{10}$, the action of nickel oxide being analogous.

From the mixture of oxides obtained by heating uranyl acetate, the sulphide UO_2S was isolated. A. McK.

Compound Thiocyanates of Palladium. ITALO BELLUCCI (*Atti R. Accad. Lincei*, 1904, [v], **13**, ii, 386—393).—Palladium resembles platinum in forming double thiocyanates of the form $Pd(SCN)_4X_2$, but the corresponding compounds derived from quadrivalent palladium either do not exist or are unstable, and when attempts are made to prepare them the bivalent palladium compounds are always obtained.

Palladous thiocyanate, $Pd(SCN)_2$, forms a reddish, flocculent precipitate, which dissolves readily in potassium thiocyanate solution yielding *potassium palladothiocyanate*, $Pd(SCN)_4K_2$, separating from water in ruby-red, acicular crystals. This double salt, which is best obtained from potassium palladochloride (1 mol.) and potassium thiocyanate (4 mols.), is a true complex salt, as is seen from a comparison of the electrical conductivity of its solutions with that of the corresponding platinum compound.

Silver palladothiocyanate, $Pd(SCN)_4Ag_2$, is an insoluble, amorphous, red salt, whilst the *barium* salt is crystalline and very readily soluble in water. The free acid is unstable and could not be prepared.

T. H. P.

5-Methylbarbituric Acid. EMIL FISCHER (*Annalen*, 1904, **336**, 345. Compare this vol., i, 37).—5-Methylbarbituric acid has been previously described as *iso*succinic-ureide by Franchimont and Klobbie (Abstr., 1888, 1181). G. Y.

Attempts to Synthesise Nitroacetonitrile. WILHELM STEINKOPF (*Ber.*, 1904, **37**, 4623—4627. Compare Ratz, Abstr., 1904, i, 857).—An attempt was made to prepare ethyl nitroacetate by distilling potassium ethyl malonate, $CO_2Et\cdot CHCl\cdot CO_2K$, with aqueous potassium nitrite, but the principal product was simply ethyl chloroacetate formed by the decomposition of the malonate by water. Nitroacetamide (Ratz, *loc. cit.*) was obtained by heating Bouveault and Wahl's nitroacetic acid (Abstr., 1904, i, 795) in the form of its ammonium salt with concentrated alcoholic ammonia for 2 hours at 100°; the immediate product is ammonium nitroacetamide, $C_2H_7O_3N_3$,

which crystallises in long, yellow needles, melts at 152°, and on treatment with dilute sulphuric acid liberates nitroacetamide, melting at 101—102°; Ratz gives the melting points for these two substances as 148° and 98°, but the author, by using Ratz's method, obtained products identical in melting point with his own. W. A. D.

Monomethyl-tin Derivatives. III. Paul Pfeiffer [with Ida Heller] (*Ber.*, 1904, **37**, 4618—4620. Compare Abstr., 1903, i, 470, 802, and Pope and Peachey, *ibid.*, 741).—Methylstanniodoform (tinmethyl iodide), $SnMeI_3$, is readily obtained by heating stannous iodide with methyl iodide for 4 hours at 160°; the best method of preparing it, however, consists in boiling an ethereal solution of magnesium methyl iodide with stannic iodide. W. A. D.

Preparation of Cyanides from Ferrocyanides. Grossman's Cyanide Patents Syndicate (D.R.-P. 156397. Compare Abstr., 1904, 562, 860).—The iron alkali ferrocyanide ("Everitt's salt"), obtained in the preparation of hydrogen cyanide from ferrocyanides, may be oxidised to Prussian blue and then decomposed by an alkali in order to recover the ferrocyanide. The oxidation, however, proceeds with difficulty with the usual oxidising agents. When air is blown into the solution, oxidation takes place rapidly. The reaction is best carried out by adding a ferrous salt and passing a current of air through the boiling solution. The oxidation takes place quantitatively, and the ferrous salt is continually regenerated: $3Na_2Fe_2Cy_6 + 2Fe_2Cl_6 = Fe_7Cy_{18} + 3FeCl_2 + 6NaCl$. C. H. D.

Preparation of Sodium Ferrocyanide from Calcium Ferrocyanide. Administration der Minen von Buchsweiler (D.R.-P. 155806).—In the preparation of potassium ferrocyanide from a solution of calcium ferrocyanide, one-half of the calcium may be replaced by the addition of potassium chloride, the sparingly soluble double salt, $K_2CaFe(CN)_6$, being precipitated. Sodium does not form a similar salt, and the addition of sodium hydroxide or carbonate has therefore been necessary to remove the calcium. It is, however, possible to separate the sodium ferrocyanide and calcium chloride, formed according to the equation $Ca_2Fe(CN)_6 + 4NaCl = Na_4Fe(CN)_6 + 2CaCl_2$, by crystallisation, the calcium chloride remaining in solution. The sodium ferrocyanide is not decomposed during evaporation. C. H. D.

New Additive Compounds of Tetrahydrobenzene. Léon Brunel (*Compt. rend.*, 1904, **139**, 1029—1031. Compare Abstr., 1903, i, 157, 338).—o-*Iodo*cyclo*hexyl acetate*, $C_6H_{10}I\cdot OAc$, obtained by the action of mercuric oxide, iodine, and acetic anhydride on *cyclo*hexene in ethereal solution, is a yellow oil with an aromatic odour, soluble in the ordinary organic solvents, has a sp. gr. 1·61 at 0°, and decomposes when distilled under reduced pressure. o-*Iodo*cyclo*hexyl propionate*, $C_6H_{10}I\cdot CO_2Et$, similarly prepared, is a yellow oil having a sp. gr. 1·64 at 0°.

The mercuric oxide and acid anhydride in the above reactions can be replaced by the mercuric salt of the corresponding acid.

M. A. W.

Preparation of Benzene free from Sulphur. CARL SCHWALBE (*Zeit. Farb. Text. Ind.*, 1904, **3**, 461—464).—The carbon disulphide present in commercially purified benzene is best removed by passing moist gaseous ammonia through the hydrocarbon, and subsequently washing it with dilute sulphuric acid. The thiophen is most completely eliminated by passing nitrous fumes, from sodium nitrite and sulphuric acid, through the liquid, and subsequently shaking it two or three times with concentrated sulphuric acid. Shaking the oil with sulphuric acid containing nitrous fumes is not so advantageous.

W. A. D.

o-Chloro-m-nitrotoluene-ω-sulphonic Acid. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 154493).—Sodium hydrogen sulphite converts *o*-chlorobenzyl chloride into *o*-chlorotoluene-ω-sulphonic acid, the sodium salt of which crystallises in glistening leaflets. On nitrating in sulphuric acid solution, *o-chloro-m-nitrotoluene-ω-sulphonic acid* is obtained. The *sodium* salt crystallises from hot water in yellow needles. The chlorine atom is readily displaced by ammonia or amines.

Permanganates oxidise the acid to 2-chloro-5-nitrobenzoic acid.

C. H. D.

Separation of Toluene-o- and -p-sulphonamides. RUDOLF BARGE & LÉON GIVANDAN (D.R.-P. 154655).—Ammonium salts may be employed in place of acids or acid salts to precipitate toluene-*o*- and -*p*-sulphonamides from the solutions of their alkali salts :

$$C_6H_4Me\cdot SO_2\cdot NHNa + NH_4Cl = C_6H_4Me\cdot SO_2\cdot NH_2 + NH_3 + NaCl.$$

A better fractional separation is obtained than when acids are used. The ammonium chloride solution obtained in the preparation of the sulphonamides from the sulphonic chlorides may be employed, and the ammonia produced may be recovered. C. H. D.

Dibromoanthracene Tetrabromide. FELIX KAUFLER and M. IMHOFF (*Ber.*, 1904, **37**, 4706—4709).—The difference in melting point between the bromoanthraquinone, prepared by Graebe and Liebermann from tribromoanthracene, and the β-bromoanthraquinone, prepared from β-aminoanthraquinone (Abstr., 1904, i, 256), is due to the presence of 2 : 6 : 9 : 10-tetrabromoanthracene in the former product.

Tetrabromoanthracene, prepared by heating dibromoanthracene tetrabromide at 200° until the evolution of bromine and hydrogen bromide ceased, melts at 298—300°, and, when oxidised in glacial acetic acid solution by chromic acid, forms *dibromoanthraquinone*, which melts at 289—290°. During the preparation of tetrabromoanthracene, tribromoanthracene was also formed. The bromoanthraquinone, prepared by oxidising the latter, melted at 201—202° and was identical with the β-compound, obtained from β-aminoanthraquinone by the diazo-reaction.

2 : 6-Diaminoanthraquinone was converted into 2 : 6-anthraquinone-

tetrazonium perbromide, which, when heated at 170°, formed 2 : 6-dibromoanthraquinone, identical with the product obtained from dibromoanthracene tetrabromide. The bromine atoms in the tetrabromoanthracene described are accordingly in the 2 : 6 : 9 : 10-position.

A. McK.

Separation of the Three Dimethylanthracenes obtained in the Action of Methylene Chloride and Aluminium Chloride on Toluene. James Lavaux (*Compt. rend.*, 1905, **140**, 44—45. Compare this vol., i, 43).—Experimental details connected with the working up of the products of the reaction are communicated, for which the original must be consulted. The three dimethylanthracenes, which are simply referred to as *A*, *B*, and *C*, melt respectively at 240°, 244·5°, and 86°.

H. M. D.

Ullmann and Borsum's "Hexaphenylethane"; Tervalency of Carbon. Alexei E. Tschitschibabin (*Ber.*, 1904, **37**, 4709—4715).—The constitution of the hydrocarbon described by Ullmann and Borsum as hexaphenylethane (Abstr., 1902, i, 755) is discussed. If this hydrocarbon were hexaphenylethane, it should undergo oxidation to triphenylcarbinol, which it does not do. Further, its formation takes place under abnormal conditions where the presence of condensing agents is necessary. The author supposes that the hydrocarbon in question is not hexaphenylethane, but diphenylmethyl-tetraphenylmethane, formed in accordance with the equation $CPh_3{\cdot}OH + C_6H_5{\cdot}CHPh_2 = CPh_3{\cdot}C_6H_4{\cdot}CHPh_2 + H_2O$. Evidence for this view is afforded by the action of bromine on the hydrocarbon, which is proved to contain one hydrogen atom, combined like the hydrogen atom of the (CH) group in triphenylmethane.

This result makes it more probable than before that Gomberg's triphenylmethyl is in reality hexaphenylethane, especially since Gomberg himself has shown that his hydrocarbon has a molecular weight double that corresponding with triphenylmethyl.

Bromine was gradually added in direct sunlight to a solution of Ullmann and Borsum's hydrocarbon in carbon disulphide. Only one molecular proportion of bromine interacted, and the *monobromide* was produced in almost quantitative yield as faintly yellowish-red crystals melting at 240—242°. This compound resembles triphenylbromomethane and reacts readily with water, alcohol, and acetic acid respectively, its action with water being represented as follows: $CPh_3{\cdot}C_6H_4{\cdot}CPh_2Br + H_2O = CPh_3{\cdot}C_6H_4{\cdot}CPh_2{\cdot}OH + HBr$. The latter reaction proceeds quantitatively when the solution of the bromide in pyridine is decomposed by hot water, the *carbinol*, $CPh_3{\cdot}C_6H_4{\cdot}CPh_2{\cdot}OH$, separating as a white powder, which crystallises from a mixture of benzene and light petroleum in glistening balls and melts at 220—220·5°. It forms a brownish-red solution with concentrated sulphuric acid, differing in this respect from the original hydrocarbon.

A. McK.

Nitrophenylcyanamides. Paul Pierron (*Bull. Soc. chim.*, 1905, [iii], **33**, 69—74).—o-*Nitrophenylcyanamide*, $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}CN$, ob-

tained by heating in closed vessels cyanogen bromide dissolved in water with *o*-nitroaniline in alcohol, crystallises in bright yellow needles, melts at 146°, is readily soluble in alcohol, and fairly so in ether. The *benzoyl* derivative crystallises in almost colourless needles from alcohol and melts at 105°.

m-*Nitrophenylcyanamide*, prepared by boiling together cyanogen bromide and *m*-nitroaniline dissolved in a mixture of water and alcohol, crystallises in short, pale yellow needles, melts at 130°, and is soluble in alcohol, less so in ether or benzene. The *benzoyl* derivative crystallises in pale yellow lamellæ, melts at 109°, and is soluble in alcohol or ether and less so in benzene.

p-*Nitrophenylcyanamide*, similarly prepared, crystallises in bright yellow needles, melts at 180°, and probably polymerises at the same time. It is very soluble in alcohol, less so in ether, and slightly so in benzene. The *benzoyl* derivative crystallises in almost colourless lamellæ, melts at 131°, and is less soluble in alcohol than its isomerides.

p-*Nitrophenylcarbamide*, obtained by heating the cyanamide, dissolved in alcohol, with hydrochloric acid, forms short prisms when crystallised by cooling a concentrated solution in alcohol and separates in needles from alcohol at 40°; it melts at 238°, is soluble in alcohol, and slightly so in benzene or ether. On reduction with tin and hydrochloric acid, it yields *p*-aminophenylcarbamide (m. p. 129°), and when heated with hydrochloric acid for from 10 to 12 hours furnishes *p*-nitroaniline. T. A. H.

Preparation of *o*-Chlorophenol. WILHELM LOSSEN (D.R.-P. 155631. Compare Hazard-Flamand, Abstr., 1903, i, 622).—Phenol may be directly chlorinated at a low temperature in an indifferent solvent, such as carbon tetrachloride, chloroform, or a liquid hydrocarbon. Solutions of phenol and chlorine may be mixed or a current of gaseous chlorine may be employed. The pure *o*-chlorophenol is isolated from the product in the usual manner. C. H. D.

Picrolonates derived from Substances [Amines] of Physiological Importance. J. OTORI (*Zeit. physiol. Chem.*, 1904, **43**, 305—315. Compare Knorr and Mathes, Abstr., 1899, i, 462; Steudel, *ibid.*, 1903, i, 431).—*Pentamethylenediamine picrolonate*, $C_5H_{10}(NH_2)_2,2C_{10}H_8O_5N_4$, obtained by mixing alcoholic solutions of the acid and of the hydrochloride of the base, crystallises in slender, orange-yellow needles or plates, begins to turn brown at 220°, and decomposes sharply at 250°. One part dissolves in 7575 of water at 16° or 357 at 100°, and in 5952 parts of cold or 475 of boiling alcohol. When prepared from the carbonate of the base, it decomposes at the same temperature, 250°, but differs as regards its solubility.

Tetramethylenediamine picrolonate crystallises in yellow needles, decomposes at 263° when slowly heated, and is very sparingly soluble. One part dissolves in 13,157 parts of cold or in 653 parts of hot water; also in 17,857 parts of cold or 954 of hot alcohol.

Picrolonate of	No. of molecules of acid combined with one of base.	Decomposes at	One part dissolves in			
			Water.		Alcohol.	
			Cold.	Boiling.	Cold.	Boiling.
Methylamine	2	244°	1073	369	4717	133
Dimethylamine	1	222	764	33	853	38
Trimethylamine	1	250—252	1121	166	794	223
Ethylamine	1	244	3846	93	1700	76
Diethylamine from hydrochloride	1	260	3788	402	2941	213
Diethylamine from carbonate...	1	260	1984	276	2193	297
Triethylamine	1	160	536	63	494	87
Betaine	1	200 (or from carbonate at 192°)	—	—	—	—
Choline........................	$1 + 1H_2O$	melts at 158°, decomposes at 241—245°	—	—	—	—
Neurine	1	233	—	—	—	—
Lysine	1	246—252	—	readily	soluble	—

J. J. S.

Alkyl Ethers of *p*-Allylphenol. Albert Verley (D.R.-P. 154654).—*p*-Bromoanisole and its homologues react with magnesium in ethereal solution to form compounds having the constitution $OMe\cdot C_6H_4\cdot MgBr$, which then react with allyl haloids forming *p*-allylanisole and its homologues.

p-*Allylanisole*, $OMe\cdot C_6H_4\cdot C_3H_5$, boils at 108—114° under 25 mm. pressure, and is converted into the propenyl compound, anethole, by boiling with alcoholic potassium hydroxide. p-*Allylphenetole* boils at 113—114° under 20 mm. and at 224° under 750 mm. pressure; *p*-propenylphenetole boils at 241° under 750 mm. pressure and melts at 61°. C. H. D.

[**4-Phenoxy-2-aminobenzenesulphonic Acid.**] Badische Anilin- & Soda-Fabrik (D.R.-P. 156156).—On heating a solution of sodium 4-chloro-3-nitrobenzenesulphonate and sodium phenoxide, *sodium 4-phenoxy-2-nitrobenzenesulphonate*, $OPh\cdot C_6H_3(NO_2)\cdot SO_3Na$, is produced. It yields on reduction 4-*phenoxy-2-aminobenzenesulphonic acid*, crystallising from water in glistening, white leaflets. The *diazo*-compound is stable and dissolves sparingly in water; it yields a red azo-dye with β-naphthol. C. H. D.

Aminoacetylcatechol. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 155632).—Aminoacetylcatechol may be prepared by

the method employed for the preparation of its alkyl derivatives (Abstr., 1904, i, 873), ammonia being used in place of alkylamines. Chloroacetylcatechol at first combines with ammonia to form the sparingly soluble ammonium salt, which then passes spontaneously into the amino-compound, which is isolated in the form of its hydrochloride.

Aminoacetylcatechol, $C_6H_3(OH)_2{\cdot}CO{\cdot}CH_2{\cdot}NH_2$, forms a crystalline powder, dissolving sparingly in water, alcohol, or ether. The *hydrochloride* crystallises from alcohol in colourless leaflets, decomposing at 260°, and dissolves readily in water. C. H. D.

[Alkyl Ethers of *o*-Tolylcarbinol.] FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 154658).—Chloromethyl alkyl ethers react with the double compounds of magnesium benzyl haloids and benzyl ether, forming alkyl ethers of *o*-tolylcarbinol:

$$CH_2Cl{\cdot}OR + Cl{\cdot}Mg{\cdot}CH_2Ph = MgCl_2 + C_6H_4Me{\cdot}CH_2{\cdot}OR.$$

o-*Tolylcarbinyl methyl ether*, $C_6H_4Me{\cdot}CH_2{\cdot}OMe$, is a colourless oil with aromatic odour and boils at 187—188°. The *ethyl ether* boils at 202—203°; the *amyl ether* boils at 124° under 15 mm. pressure.

C. H. D.

[Colourless Salts of Triphenylcarbinol and Diphenylcarbinol.] RUDOLF LAMBRECHT and HUGO WEIL (*Ber.*, 1904, **37**, 4647).—An historical correction (compare *Ber.*, 1904, **37**, 3058). W. A. D.

Action of Light on Cholesterol. ERNST SCHULZE and ERNST WINTERSTEIN (*Zeit. physiol. Chem.*, 1904, **43**, 316—319).—When cholesterol is exposed to bright sunlight for some time, it turns yellow, its melting point is considerably lowered, and it ceases to give the characteristic reactions with acetic anhydride and sulphuric acid or with vanillin and hydrochloric acid. All these changes are due to the formation of a small amount of brownish-yellow substance, which remains in the mother liquor when the cholesterol is crystallised from alcohol. Cholesterol is not affected when sealed in a glass tube containing carbon dioxide and then exposed to light. J. J. S.

Cholesterol. IV. ADOLF WINDAUS (*Ber.*, 1904, **37**, 4753—4756. Compare Abstr., 1904, i, 49, 667 and 1010. Compare Diels and Abderhalden, *ibid.*, 880).—Bromocholestanonic acid (Abstr., 1904, i, 667), when heated with glacial acetic acid containing hydrochloric acid, is converted into the *lactone*, $C_{27}H_{40}O_5$, of a hydroxycholestanonic acid; the lactone crystallises from alcohol in long needles, melts after sintering at 192—193°, and behaves on titration with cold aqueous sodium hydroxide as a monobasic acid, but with the hot alkali as a dibasic acid. On heating the lactone-acid with 10 per cent. aqueous potassium hydroxide for two hours, it is transformed into a *hydroxyketodicarboxylic acid*, $C_{27}H_{42}O_6$, which crystallises from diluted acetic acid, melts at 174—175°, and, as it does not give a lactone, is isomeric with the acid corresponding to the lactone just described. This acid

can be readily obtained by heating bromocholestanonic acid directly with aqueous potassium hydroxide; as it is very resistant to chromic acid, it probably contains a tertiary hydroxyl radicle. W. A. D.

Dehydration of *a-iso*Dypnopinacolin. I. ÉGIDE TERLINCK (*Bull. Acad. Roy. Belg.*, 1904, 1049—1086. Compare Delacre and Gesché, Abstr., 1904, i, 32).—The first part of the paper gives detailed descriptions of methods for the preparation and isolation of *a-iso*-dypnopinacolin, homodypnopinacolin, and the hydrocarbon, $C_{25}H_{22}$, from dypnone or acetophenone (compare Delacre, Abstr., 1896, i, 591; 1900, i, 603, and Gesché, 1900, i, 604; 1903, i, 484).

By the dehydration of *a-iso*dypnopinacolin, the *a*- and *β-iso*dypno-pinacolenes, $C_{32}H_{24}$, are formed (compare Delacre, Abstr., 1896, i, 591). The dehydration may be brought about by mixtures of acetic acid with sulphuric, hydrochloric, or hydrobromic acid, or by acetyl chloride. The relative amounts of the two isomerides formed varies with the nature of the dehydrating agent employed, a "strong" acid favouring the production of *β-iso*dypnopinacolene (m. p. 171°) and a feeble one the formation of the isomeride. No evidence of the conversion of one isomeride into the other by the action of these dehydrating agents was obtained. *a-iso*Dypnopinacolene crystallises from acetic acid or alcohol in lamellæ, melts at 175·5°, and distils under atmospheric pressure with the formation of a small quantity of the *β* isomeride. When heated with potassium hydroxide at 220°, it is converted into a *product*, $C_{32}H_{20}O$, which crystallises from chloroform on addition of ether in needles or parallelopipeds and melts at 173°. With sulphuric acid, there is formed a *derivative* (sulphonic?) which crystallises in white spangles and is soluble in water, from which it is reprecipitated by ammonium chloride. Nitric acid, acting on *a-iso*dypnopinacolene dissolved in acetic acid, converts it into a *nitro*-derivative, $C_{32}H_{23}O_2N$; this crystallises from dilute acetic acid or nitrobenzene in hard, yellow crystals and melts at 272°. On reduction, *a-iso*dypnopinacolene does not yield definite products, but on oxidation by chromic acid in presence of acetic acid a small quantity of benzoic acid is formed.

When the hydrocarbon is dissolved in carbon disulphide and treated with a molecular proportion of bromine, a *bromo*-derivative, $C_{32}H_{25}Br$, is produced, which crystallises in pale yellow needles, melts at 199—200°, and on reduction with sodium amalgam in presence of alkalis furnishes a series of crystalline products. When chloroform is employed as the solvent, an isomeric *bromo*-derivative is obtained; this crystallises in tablets, melts at 192°, and furnishes a crystalline reduction product with sodium amalgam. When the bromination is carried out in presence of acetic acid, a crystalline product of indefinite composition is formed. A *dibromo*-derivative forming large, cubical crystals is obtained when bromine (2 mols.) is added to *a-iso*dypnopina-colene dissolved in carbon disulphide. When the hydrocarbon is mixed with reduced iron and excess of bromine added, a vigorous reaction ensues and the principal product is the *compound* $C_{32}H_{14}Br_{10}$; this crystallises from chloroform on addition of ether in straw-coloured tablets, retains chloroform tenaciously, develops a violet colour on exposure to sunlight, evolves hydrogen bromide and becomes resinous

when heated, and when warmed with potassium hydroxide in alcohol furnishes a bright red solution. T. A. H.

Constitution of Anthranil. GUSTAV HELLER (*J. pr. Chem.*, 1904, [ii], **70**, 516—520. Compare Abstr., 1902, i, 779; 1903, i, 827; 1904, i, 160).—A reply to Bamberger (Abstr., 1904, i, 422). G. Y.

Chloralamino-compounds. II. SIMON GÄRTNER (*Annalen*, 1904, **336**, 229—246. Compare Abstr., 1904, i, 788).—Trichloroethylideneanthranilic acid and potassium cyanide react in aqueous solution, at the ordinary temperature, to form a product which, when boiled with water, yields dichloroacetylanthranilic acid (Jackson, Abstr., 1881, 735); this is also formed by the action of dichloroacetic chloride on anthranilic acid; it crystallises in colourless needles or large, colourless plates, melts at 176—177°, is hydrolysed by aqueous sodium hydroxide, or, less easily, by dilute sulphuric acid, to anthranilic, dichloroacetic, and glycollic acids, and is reduced by sodium amalgam in aqueous solution to anthranilic acid. The *silver* salt,

$$C_9H_6O_3NCl_2Ag,$$

crystallises in rosettes of needles; the *ethyl* ester, $C_{11}H_{11}O_3NCl_2$, crystallises in rhombic plates, melts at 58—60°, and boils at 180—190° under 13 mm. pressure. The *silver*, *barium*, and *calcium* salts of anthranilic acid are described.

When boiled with acetic anhydride, dichloroacetylanthranilic acid forms the *lactone* of its tautomeric form, $C_6H_4<\begin{matrix}N{=}C\cdot CHCl_2\\ CO\cdot O\end{matrix}$, which crystallises in long, colourless prisms, melts at 175°, is easily soluble in acetone or chloroform, and is hydrolysed, when boiled with water, to the dichloro-acid. When boiled with 20 per cent. ammonia in a reflux apparatus, the lactone forms dichloroacetylanthranilimine (4-keto-2-dichloromethyldihydroquinazoline), $C_6H_4<\begin{matrix}N{=}C\cdot CHCl_2\\ CO\cdot NH\end{matrix}$, which crystallises in thick rhombohedra, melts at 210°, sublimes without decomposition, and, when dissolved in warm aqueous sodium hydroxide, is converted into an *amino*-acid. The action of phenylhydrazine on the lactone leads to the formation of two substances: a *chloro*-compound, $C_{21}H_{18}ON_5Cl$, which crystallises in red plates and melts and decomposes at 248°, and a *derivative*, $C_{21}H_{17}ON_5$, which crystallises in glistening needles and melts and partly decomposes at 232°. G. Y.

ω-Sulphomethylanthranilic Acid. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 155628).—Formaldehyde and anthranilic acid combine in aqueous suspension or ethereal solution to form a condensation product, separating in yellowish-white crystals melting at about 145—150°, insoluble in water or dilute acids, readily soluble in acetone. The compound becomes luminous on rubbing. Sodium sulphite converts it into *ω-sulphomethylanthranilic acid* (sulphite compound of methyleneanthranilic acid), which reacts with metallic cyanides to form ω-cyanomethylanthranilic acid (compare Abstr., 1903, i, 336). C. H. D.

α-Amino-acids. EMIL ERLENMEYER, jun. (*Annalen*, 1904, **337**, 205—221).—An account is given of the various methods of preparing α-amino-acids, including some recent and new methods devised by the author, in which aldehydes are condensed with glycine and analogous substances. The synthesis of α-amino-β-hydroxy-acids by similar methods is also described. The paper concludes with a discussion of the state of our knowledge of the property exhibited by the methylene group of inducing condensation with various substances.

K. J. P. O.

Synthesis of some α-Amino-β-hydroxy-acids. EMIL ERLENMEYER, jun., and F. BADE (*Annalen*, 1904, **337**, 222—235. Compare preceding abstract).—The number of aldehydes which are able to condense with glycine forming α-amino-β-hydroxy-acids is very limited. Neither vanillin nor salicylaldehyde will condense in this manner. *o*-Methoxybenzaldehyde (2 mols.), however, condenses with glycine (1 mol.) when they are shaken together in the presence of a 50 per cent. solution of sodium hydroxide to which alcohol has been added; the product solidifies, a mixture of two substances being formed which are separated by crystallisation from alcohol. The less soluble is the *sodium* salt, $OMe\cdot C_6H_4\cdot CH(OH)\cdot C(N\colon CH\cdot C_6H_4\cdot OMe)\cdot CO_2Na,\frac{1}{2}EtOH$, which forms rhombs. The free acid could not be obtained, but its *acetyl* derivative, $OMe\cdot C_6H_4\cdot CH(OAc)\cdot C(N\colon CH\cdot C_6H_4\cdot OMe)\cdot CO_2H,H_2O$, is obtained, together with a neutral yellow substance, when the sodium salt is heated with acetic anhydride at 100°; it forms crystals, becoming yellow at 210° and decomposing at 216°. When a solution of the sodium salt is treated with dilute acetic acid, o-*methoxyphenylserine*, $OMe\cdot C_6H_4\cdot CH(OH)\cdot CH(NH_2)\cdot CO_2H,H_2O$, is obtained, *o*-methoxybenzaldehyde being eliminated; this acid crystallises in leaflets very soluble in water, and melting and decomposing at 179°; the *hydrochloride* is a crystalline powder, and the *copper* salt a greyish-blue, insoluble powder. When heated with acetic anhydride, the amino-acid is converted into the *oxazole*, $OMe\cdot C_6H_4\cdot CH\colon C<\begin{matrix}N{=}CMe\\ CO\cdot O\end{matrix}$, which crystallises in yellow leaflets melting at 156°; it is identical with the yellow substance formed when the sodium salt is heated with acetic anhydride. On boiling the oxazole with sodium hydroxide, it is converted into the *acid*, $OMe\cdot C_6H_4\cdot CH\colon C(NHAc)\cdot CO_2H$, which crystallises in small needles melting and decomposing at 214°.

The soluble substance formed in the condensation is best prepared by using 3 mols. of the *o*-methoxybenzaldehyde, and is a compound formed by condensation of 3 mols. of the aldehyde with glycine, $OMe\cdot C_6H_4\cdot CH(OH)\cdot CH(C_6H_4\cdot OMe)\cdot N\colon CH\cdot C_6H_4\cdot OMe$; it crystallises in needles melting at 134°, and in alcohol gives an alkaline reaction. When heated with acetic anhydride, it yields an *acetyl* derivative melting at 170°. On warming with hydrochloric acid at 100°, the free *base*, $OMe\cdot C_6H_4\cdot CH(OH)\cdot CH(NH_2)\cdot C_6H_4\cdot OMe$, is obtained, crystallising in needles melting at 136°; the *platinichloride* crystallises from alcohol and melts at 197°. When heated, the base decomposes into *o*-methoxybenzaldehyde and o-*methoxybenzylamine* (o-*anisamine*), which is an oil; the *hydrochloride* crystallises in long needles melting

at 149°, and the *platinichloride*, $(C_8H_{11}ON)_2,H_2PtCl_6,2\frac{1}{2}H_2O$, in dark yellow leaflets melting and decomposing at 189°. K. J. P. O.

Unsaturated Compounds. II. F. WILLY HINRICHSEN (*Annalen*, 1904, **336**, 323—344. Compare Abstr., 1902, i, 129; 1904, i, 1012).—[With OSCAR LOHSE.]—When acted on by bromine in chloroform solution, ethyl α-cyanocinnamenylacrylate forms a *di*bromide,

$$CHPhBr\cdot CHBr\cdot CH{:}C(CN)\cdot CO_2Et,$$

which melts at 98°, and is oxidised by chromic acid in glacial acetic acid solution to the dibromide of cinnamic acid. The *dibromide* of cyanocinnamenylacrylic acid melts at 187° and yields the ethyl ester melting at 98°.

Cinnamylidenemalononitrile, $CHPh{:}CH\cdot CH{:}C(CN)_2$, obtained by the condensation of cinnamaldehyde with methylene dicyanide in presence of sodium ethoxide, crystallises in slender, yellow needles, melts at 128°, and forms a white, crystalline dibromide,

$$CHPhBr\cdot CHBr\cdot CH{:}C(CN)_2,$$

which melts at 130°, and, on oxidation, yields benzoic and dibromohydrocinnamic acids.

[With MARIE REIMER.]—When oxidised with potassium permanganate in acetone solution, methyl α-nitrophenylcinnamenylacrylate yields dibromohydrocinnamic acid, *p*-nitrobenzoic acid, and an acid which melts at 110—120° and may be phenylbromolactic acid.

[With OSCAR LOHSE.]—Cinnamaldehyde neither reacts in presence of sodium ethoxide with a methyl group except in the cases of acetone and acetophenone, nor with methylene unless it is combined with two nitrile groups or with one nitrile and one other slightly acid group. Other aldehydes also take part in the reaction. The following new substances prepared by this reaction are described:

α-Cyanocitrylideneacetic acid, $C_{13}H_{17}O_2N$, obtained by the action of citral on ethyl cyanoacetate, and hydrolysis of the product, forms small, yellow crystals and melts at 150°.

o-*Hydroxybenzylidenemalononitrile*, $OH\cdot C_6H_4\cdot CH{:}C(CN)_2$, obtained from salicylaldehyde and malononitrile, forms yellow crystals and melts at 183—184°.

Methoxybenzylidenemalononitrile, $OMe\cdot C_6H_4\cdot CH{:}C(CN)_2$, from anisaldehyde and malononitrile, crystallises in slender, white needles and melts at 110°.

On addition of sodium ethoxide to the alcoholic solution of cinnamaldehyde and chloroacetonitrile, a precipitate of sodium chloride is formed, and a dark oil is obtained on evaporation of the alcohol.

G. Y.

Isomeric Esters of Orthoketo-acids. GUIDO GOLDSCHMIEDT and ALFRED LIPSCHITZ (*Monatsh.*, 1904, **25**, 1164—1176. Compare Abstr., 1904, i, 168; Meyer, Abstr., 1904, i, 747).—When heated with acetic anhydride, *o*-fluorenoylbenzoic acid forms an *acetyl* derivative which crystallises in matted, white needles, sinters at 120°, and melts and is converted into fluorenoylbenzoic anhydride at 150—160°. The oxime of the anhydride melts and decomposes at 237—238°, is insoluble in dilute aqueous potassium hydroxide, and dissolves in concentrated sulphuric acid to a lemon-coloured solution.

Fluorenonoylbenzoic acid, obtained by oxidation of *o*-fluorenoylbenzoic acid with alkaline permanganate, is yellow and crystalline and melts at 248—250°. *Methyl fluorenonoylbenzoate*, $C_{20}H_{11}O_2 \cdot CO_2Me$, obtained by the action of methyl iodide on the silver salt or of methyl-alcoholic sulphuric acid on the acid, melts at 160—162° and dissolves in concentrated sulphuric acid to a lemon-yellow solution. An isomeric *methyl* ester is formed by warming the acid with thionyl chloride and treating the product with methyl alcohol; it melts at 184—186° and dissolves in concentrated sulphuric acid to a red solution. The *acetyl* derivative obtained by heating the acid with acetic anhydride melts at 178—180° and dissolves in concentrated sulphuric acid to a red solution.

Methyl naphthoylbenzoate, $C_7H_{11}O \cdot CO_2Me$, obtained by esterifying the acid with methyl alcohol and concentrated sulphuric acid or hydrogen chloride, by treatment of the silver salt with methyl iodide, or by the action of methyl alcohol on the acid chloride obtained by means of thionyl chloride, forms large, glistening, monoclinic crystals [$a:b:c = 1 \cdot 3561:1:1 \cdot 0897$; $\beta = 74°$], melts at 117—120°, and dissolves in concentrated sulphuric acid to an intensely yellow solution which slowly becomes red. The isomeric *methyl* ester is formed by the action of methyl alcohol on the acid chloride obtained by means of phosphorus trichloride or pentachloride; it separates from methyl alcohol in monoclinic crystals [$a:b:c = 0 \cdot 6138:1:1 \cdot 5430$; $\beta = 67°16'$], melts at 134—137°, and dissolves, as does the free acid, in concentrated sulphuric acid to a violet solution.

Ethyl fluorenonecarboxylate, which melts at 84—86° (Abstr., 1903, i, 161), is also obtained by the action of ethyl iodide on the silver salt, by esterification with alcohol and sulphuric acid, or by treatment with alcohol of the acid chloride prepared by means of phosphorus trichloride. The *methyl* ester, $C_{13}H_7O \cdot CO_2Me$, prepared by the various methods, crystallises in glistening, yellow needles, melts at 86—89°, and dissolves, like the free acid, in concentrated sulphuric acid to a red solution. No second ethyl or methyl ester of fluorenonecarboxylic acid could be obtained. G. Y.

Isomeric Esters of Aromatic-Keto-acids. HANS MEYER (*Monatsh.*, 1904, **25**, 1177—1195. Compare Abstr., 1904, i, 747; Goldschmiedt and Lipschitz, preceding abstract).—*o*-Benzoylbenzoic chloride, prepared by the action of thionyl chloride on the acid and the excess of the reagent removed by a current of dry air at 50° under reduced pressure, is a colourless, viscid oil which does not solidify when strongly cooled, or on addition of a crystal of the acid chloride which melts at 68—71°. It distils at 330—350°, decomposing into hydrogen chloride and anthraquinone, and when treated with concentrated aqueous ammonia at 0° yields the amide, which is also formed by the action of ammonia on either of the methyl esters. In the presence of aluminium chloride, the liquid acid chloride reacts with benzene to form phthalophenone.

o-Benzylbenzoic acid, prepared by Ullmann's method (Abstr., 1896, i, 563), crystallises in long needles; the silver salt crystallises in needles and, with methyl iodide, forms the methyl ester, which is also obtained by

conversion of the acid into its chloride by means of thionyl chloride and treatment of the product with methyl alcohol. It is a colourless liquid, which has a pleasant odour, and is oxidised by chromic acid to the dilactone of dihydroxytetraphenylethanedicarboxylic acid (Ullmann, *loc. cit.*). The esters of *o*-benzoylbenzoic acid are reduced by zinc and acetic acid to the lactone of benzhydrylbenzoic acid and a small amount of a less fusible product which contains no methoxy-group. The action of phenylhydrazine on the isomeric esters, in absence of a solvent, leads to the formation of Roser's phenylhydrazone (Abstr., 1885, 797), which melts at 162—163° instead of at 180—182°, as stated by that author.

Methyl *p*-toluoyl-*o*-benzoate, obtained by the action of alcohol and sulphuric acid on the acid, or of methyl sulphate on the potassium salt, melts at 61°; previous authors have given the melting point as 54° and 66°. The isomeric *methyl* ester, formed by the action of methyl alcohol on the liquid acid chloride, which is obtained by means of thionyl chloride, melts at 71—72°, is less soluble than its isomeride, and gives an intensely yellow coloration with concentrated sulphuric acid. A mixture of equal amounts of the two isomeric esters melts at 48—49°.

Methyl p-*hydroxybenzoylbenzoate*, formed by the action of sulphuric acid and methyl alcohol on the acid, melts at 134°. The isomeric *ester* obtained by the thionyl chloride method melts at 134—135° and dissolves in concentrated sulphuric acid to an intensely orange-yellow solution. A mixture of the two esters melts at 112—114°.

The methyl ester of tetrachlorobenzoylbenzoic acid, which is obtained by shaking the potassium salt with methyl sulphate in aqueous solution, crystallises in needles and melts at 92°. The chloride formed by the action of thionyl chloride on the acid is crystalline, melts at 179—180°, and, when boiled with methyl alcohol, yields the second methyl ester, which crystallises from a mixture of chloroform and methyl alcohol and melts at 154° (Kircher, Abstr., 1887, 831).

The action of diazomethane on *o*-benzoylbenzoic, *p*-toluoyl-*o*-benzoic, and tetrachlorobenzoylbenzoic acids leads to the formation of the more fusible methyl esters. It is probable that the free *o*-keto-acids and their more fusible esters, which are therefore the ψ-esters, have the lactonic constitution. G. Y.

Introduction of Nitrogen into the Santonin Molecule, and the Physiological Behaviour of Certain Santonin Derivatives. Edgar Wedekind (*Zeit. physiol. Chem.*, 1904, **43**, 240—248. Compare Abstr., 1904, i, 60).—Benzene azodesmotroposantonin (Abstr., 1903, i, 542), on reduction with stannous chloride and hydrochloric acid, yields the *hydrochloride* of d-*aminosantonous acid*,

$$\begin{array}{l} CH_2\cdot CH_2\cdot C\cdot CMe{:}C\cdot NH_2 \\ CO_2H\cdot CHMe\cdot CH-CH_2\cdot C\cdot CMe{:}C\cdot OH \end{array}.$$

It crystallises in plates, which tend to turn red on exposure to the air, is dextrorotatory, and its aqueous solutions have a strong acid reaction. The *amino-acid* crystallises from alcohol in colourless needles, melting at 206°, and is only sparingly soluble in water.

Santonin, desmotroposantonin, santonic acid, and the above hydro-

chloride have been examined from a physiological point of view. Although santonin acts as a strong poison when taken into the human system, none of these four compounds has any appreciable toxic effect on lower animals, and only santonin itself appears to be capable of destroying ascarides. J. J. S.

Glycollic Acid Derivatives of Pyrogallol and its Alkyl Ethers. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 155568).—Pyrogallol and its alkyl ethers combine with chloroacetic acid on boiling with sodium hydroxide in a reflux apparatus or in an open vessel, the volume of the solution being maintained constant. The condensation product separates on acidifying with hydrochloric acid, and may be recrystallised from water.

Pyrogallolglycollic acid, $C_6H_3(OH)_2 \cdot O \cdot CH_2 \cdot CO_2H$, melts at 153—154° and dissolves readily in alcohol or hot water, sparingly in cold water, ether, or benzene; the alkaline solution becomes brown in air. *Pyrogalloldiglycollic acid*, $OH \cdot C_6H_3(O \cdot CH_2 \cdot CO_2H)_2$, is similar, but its alkaline solution does not darken in air.

Pyrogallol ethyl ether diglycollic acid, $OEt \cdot C_6H_3(O \cdot CH_2 \cdot CO_2H)_2$, crystallises from benzene and melts at 108—109°; *pyrogallol diethyl ether glycollic acid*, $C_6H_3(OEt)_2O \cdot CH_2 \cdot CO_2H$, melts at 82—83°. The poisonous character of pyrogallol disappears in these derivatives. C. H. D.

Decomposition of Gallotannic Acid. FRANZ UTZ (*Chem. Zeit.*, 1905, **29**, 31).—When tannin is boiled with dilute hydrochloric acid, dextrose is first formed and, on further boiling, lævulose and furfuraldehyde. A. McK.

Interaction of Phenylcarbimide with 1 : 3-Dicarbonyl Compounds. WALTER DIECKMANN, J. HOPPE, and RICHARD STEIN (*Ber.*, 1904, **37**, 4627—4638. Compare Abstr., 1904, i, 847, 873).—The majority of acyclic 1 : 3-dicarbonyl compounds, for example, ethyl benzoylacetate, acetylacetone, benzoylacetone, dibenzoylmethane, and ethyl malonate, interact with phenylcarbimide giving *C*-carbanilides, according to the equation:

$$R \cdot CO \cdot CH_2 \cdot CO \cdot R' + PhN{:}CO = R \cdot CO \cdot CH(CO \cdot R') \cdot CO \cdot NHPh;$$

that the products are not *O*-carbanilides, as has been assumed previously in several cases, for instance, those of dibenzoylmethane and benzoylacetone, is shown by the fact that they have an acid character, give the ferric chloride reaction, and are hydrolysed according to Claisen's rule, exemplified by the equation:

$$CH_3 \cdot CO \cdot CHBz \cdot CO \cdot NHPh + KOH = CH_3 \cdot CO_2K + CH_2Bz \cdot CO \cdot NHPh.$$

These *C*-carbanilides, however, are produced either at the ordinary temperature or at 100° only in presence of traces of alkali, for example, that imparted by soda-glass. In the case of alkyl-substituted ethyl acetoacetates and acyclic 1 : 3-diketones, the interaction with phenylcarbimide, even in presence of alkali, takes place extraordinarily slowly, but traces of a *C*-carbanilide appear to be formed.

In all these cases, the formation of an *O*-carbanilide could not be detected. On the other hand, the dihydroresorcins, like phenols in absence of alkali, give at once *O*-carbanilides; the hydroxymethylene-compounds, however, although giving *O*-carbanilides, require the pre-

sence of traces of alkali to initiate the action. When an alkali is used in the case of the dihydroresorcins, instead of getting an *O*-carbanilide, a *C*-carbanilide is produced; an alkali transforms, for instance,

$$CO<\begin{matrix}CH{:}C(O\cdot CO\cdot NHPh)\\ CH_2\text{———————}CHPh\end{matrix}>CH_2$$

into $CO<\begin{matrix}C(CO\cdot NHPh){:}C(OH)\\ CH_2\text{—————}CHPh\end{matrix}>CH_2$, in a few minutes at 100°. The analogous transformation of the *O*-carbanilide of hydroxymethylene acetophenone into the *C*-carbanilide, $CHBz{:}CH\cdot O\cdot CO\cdot NHPh \longrightarrow OH\cdot CH{:}CBz\cdot CO\cdot NHPh$, can be effected by heating it in ethereal solution with dry potassium carbonate. In the case of phloroglucinol, no interaction with phenylcarbimide occurs at 100° when an alkali is absent; the addition of a trace of sodium carbonate gives rise to a substance which, differing from Goldschmidt's tricarbanilide, is undoubtedly the *O*-tricarbanilide.

These facts show that the use of phenylcarbimide in ascertaining the structure of isodynamic substances is subject to considerable limitations. The new compounds obtained in investigating the foregoing cases are as follows:

Ethyl benzoylmalonanilate, $OH\cdot CPh{:}C(CO_2Et)\cdot CO\cdot NHPh$, obtained from ethyl benzoylacetate and phenylcarbimide, crystallises from alcohol in colourless needles and melts at 142—143°; on hydrolysis with alcoholic potassium hydroxide, it gives benzoic acid and malonanilic acid.

Ethyl acetylbenzylmalonanilate, $CH_2Ph\cdot CAc(CO_2Et)\cdot CO\cdot NHPh$, could not be isolated in the case of the interaction of ethyl benzylacetoacetate with phenylcarbimide, but its formation is evident from the fact that the product on hydrolysis gives *a-carboxydihydrocinnamanilide*, $CH_2Ph\cdot CH(CO_2H)\cdot CO\cdot NHPh$, which crystallises from alcohol in colourless needles and decomposes on melting, giving dihydrocinnamanilide; the latter melts at 97°, not at 92° as previously stated.

Diacetylacetanilide, $CHAc_2\cdot CO\cdot NHPh$, prepared from acetylacetone, crystallises from alcohol in colourless needles and melts at 117—119°. *Benzoylacetylacetanilide*, $CH_3\cdot C(OH){:}CBz\cdot CO\cdot NHPh$, obtained from benzoylacetone, forms colourless needles, melts at 126°, and on hydrolysis gives benzoylacetanilide. Dibenzoylacetanilide,

$$CHBz_2\cdot CO\cdot NHPh,$$

obtained by the action of phenylcarbimide on dibenzoylmethane, gives on hydrolysis benzoic acid and benzoylacetanilide.

Dicarbethoxyacetanilide (ethyl *C*-carbanilinomalonate),

$$CH(CO_2Et)_2\cdot CO\cdot NHPh,$$

separates from alcohol in colourless crystals, melts at 122°, and, on hydrolysis, gives malonic acid monanilide.

The O-*carbanilide* of dimethyldihydroresorcin,

$$CO<\begin{matrix}CH{:}C(O\cdot CO\cdot NHPh)\\ CH_2\text{———————}CMe_2\end{matrix}>CH_2,$$

crystallises from benzene in colourless needles, melts at 105—106°, and on hydrolysis gives methyl phenylcarbamate and dimethyldihydroresorcin.

Dimethyldihydroresorcin C-*carbanilide*,

$$CO<\begin{matrix}C(CO\cdot NHPh){:}C(OH)\\ CH_2\text{———————}CMe_2\end{matrix}>CH_2,$$

crystallises from alcohol, melts at 93—94°, and is not attacked by methyl alcoholic potassium hydroxide.

Phenyldihydroresorcin O-carbanilide,

$$CO<\begin{matrix}CH:C(O\cdot CO\cdot NHPh)\\CH_2 \text{———} CHPh\end{matrix}>CH_2,$$

crystallises from benzene and melts between 130° and 184°, decomposing into its components. The *C-carbanilide,*

$$CO<\begin{matrix}C(CO\cdot NHPh):C(OH)\\CH_2 \text{———} CHPh\end{matrix}>CH_2,$$

melts at 136° and is not hydrolysed by alcoholic potassium hydroxide. The isomeric *C-carbanilide,* $CO<\begin{matrix}CH:C(OH)\\CH_2\cdot CHPh\end{matrix}>CH\cdot CO\cdot NHPh$, obtained from ethyl cinnamate and sodioacetoacetylanilide, crystallises from alcohol and melts at 196—197°.

From hydroxymethyleneacetophenone, the *O-carbanilide,*

$$CHBz:CH\cdot O\cdot CO\cdot NHPh,$$

is obtained; it crystallises from benzene in colourless needles, melts at 123—125°, and is easily hydrolysed into its constituents. The *C-carbanilide,* $NHPh\cdot CO\cdot CBz:CH\cdot OH$, crystallises from benzene, melts at 93—94°, and is only very slowly hydrolysed by alcoholic potassium hydroxide, giving then formic acid and benzoylacetanilide.

Phloroglucinol-O-tricarbanilide, $C_6H_3(O\cdot CO\cdot NHPh)_3$, crystallises from alcohol or glacial acetic acid, melts at 190—191°, and is easily hydrolysed into phloroglucinol and methyl phenylcarbamate. *Diethyl phloroglucinoldicarboxylate O-tricarbanilide,*

$$(CO_2Et)_2\cdot C_6H(O\cdot CO\cdot NHPh)_3,$$

melts at 150—155° and is also easily hydrolysed. W. A. D.

Esterification by means of Sulphuric Acid. II. Hans Meyer (*Monatsh.*, 1904, **25**, 1201—1214. Compare Abstr., 1904, i, 216).—Methyl anthranilate is formed in 92 per cent. yield when anthranilic acid is dissolved in concentrated sulphuric acid. *Methyl* p-*aminomesitylate*, formed by the same method, melts at 93°. *Methyl* o-*aminomesitylate* melts at 39° and has a slight odour resembling that of ethyl benzoate. By this method of esterification, 4 grams of hemimellitic acid yields 2·3 grams of the trimethyl and 1·2 grams of the diethyl ester. The esters were obtained in the same proportion when 5 grams of the acid were boiled with 10 grams of sulphuric acid and 50 grams of methyl alcohol (compare Graebe and Leonhardt, Abstr., 1896, i, 437; Meyer, Abstr., 1896, i, 547). When treated with thionyl chloride, dimethyl hydrogen hemimellitate is converted into its crystalline *chloride*, which melts at 84—87°, and, when treated with absolute alcohol and barium carbonate, forms the *dimethyl ethyl* ester,

$$CH<\begin{matrix}CH\cdot C(CO_2Me)\\CH:C(CO_2Me)\end{matrix}>C\cdot CO_2Et.$$

This is a colourless oil, having an odour of apples, and, when shaken with *N*-sodium hydroxide solution, yields ethyl dihydrogen hemimellitate, $CH<\begin{matrix}CH\cdot C(CO_2H)\\CH:C(CO_2H)\end{matrix}>C\cdot CO_2Et$, which crystallises in needles, melts at 175°, and is formed when hemimellitic anhydride is boiled with alcohol.

When dissolved in sulphuric acid and heated with methyl alcohol in a benzene-bath, mellitic acid forms the pentamethyl ester; at 100° a mixture of this with the hexamethyl ester is obtained, whilst at 120—125° the latter preponderates very largely. *Pentamethyl hydrogen mellitate* crystallises in long, silky, glistening needles and melts at 141—144°. G. Y.

Lichens and their Characteristic Constituents. IX. Oswald Hesse (*J. pr. Chem.*, 1904, [ii], 70, 449—502, 561. Compare Abstr., 1898, i, 378, 531, 679; 1899, i, 381; 1901, i, 85, 149, 595; 1902, i, 680; 1903, i, 702).—*Cladonia squamosa* (*C. frondosa*) was gathered from a boulder in the upper Rennbach Thal near Wildbad; as with the var. *ventricosa*, the only characteristic constituent found was squamatic acid. When treated with concentrated aqueous potassium hydroxide, this acid forms delicate, white needles, probably of the potassium salt, which gradually redissolve, when, on addition of water, the solution becomes blood-red; the *barium* salt forms a white, voluminous, flocculent precipitate.

Cladonia (*Cladina*) *destricta* contains *l*-usnic and squamatic acids, a pigment which forms a blue compound with aqueous sodium hydroxide, and an indifferent compound, *cladestin*, which forms a white, microcrystalline powder, becomes yellow at 240°, melts at 252°, and gives a dark red coloration with ferric chloride in alcoholic solution. Zopf's destrictic acid (Abstr., 1903, i, 763) was possibly squamatic acid; no trace of a colourless compound crystallising in leaflets could be found.

Cladonia furcata (*C. racemosa*, *C. recurva*) was obtained from the woods in the neighbourhood of the Waldeck Ruin, between Talmühle and Teinach stations, in Wurtemberg; it yields traces of an acid, which crystallises in small, colourless scales, and gives a red coloration with ferric chloride and a wax-like substance which is soluble in ether. *Cetraria islandica* of various origins yields proto-α-lichesteric acid, which is monobasic, forms the *barium* salt $(C_{18}H_{29}O_5)_2Ba$, and, when heated with hydriodic acid of sp. gr. 1·7, yields no alkyl iodide, but is almost entirely converted into a substance which melts at 70—80°; no lichesteric acid was obtained from the moss (Böhme, Abstr., 1903, i, 316). In the Iceland moss, fumaric acid is present in combination with protocetraric acid as fumaroprotocetraric acid, $C_{62}H_{46}O_{33},2H_2O$, previously considered to be identical with protocetraric acid (Abstr., 1898, i, 534). It crystallises in small, white needles, commences to decompose at 240°, and at 260° has become black without having melted; at higher temperatures, a sublimate of fumaric acid is formed; it is sparingly soluble in water, ether, alcohol, or acetone; the alcoholic solution has an acid reaction, and gives a purple coloration with ferric chloride; in concentrated sulphuric acid, it dissolves to a dark red solution. When dissolved in aqueous alkali hydroxide, precipitated by the addition of hydrochloric acid, and again neutralised with the alkali hydroxide, fumaroprotocetraric acid is hydrolysed to fumaric and protocetraric acids, or to diethylprotocetraric acid if the reaction takes place in alcohol. Proto-

cetraric acid, $C_{54}H_{42}O_{27}$, forms spherical, crystalline aggregates, decomposes without melting at 250°, gives a purple coloration with ferric chloride in alcoholic solution, and dissolves in concentrated sulphuric acid to a red solution. The *barium*, $(C_{54}H_{39}O_{27})_2Ba_3$, the *calcium*, $(C_{54}H_{39}O_{27})_2Ca_3$, and the yellow, amorphous *silver* salt are described. When heated with methyl alcohol in a sealed tube at 100°, protocetraric acid forms the *tri*methyl ether, $C_{54}H_{39}O_{24}(OMe)_3$, which crystallises in short, colourless prisms, becomes black at 240° without having melted, and gives a purple coloration with ferric chloride in alcoholic solution. The *potassium* salt, $C_{57}H_{45}O_{27}K_3$, is a white powder, and on treatment with warm alcoholic potassium hydroxide forms the *salt*, $C_{57}H_{43}O_{27}K_5$ which crystallises in white needles. When heated with methyl alcohol and concentrated sulphuric acid in a sealed tube at 100°, trimethylprotocetraric or fumaroprotocetraric acid yields *trimethylcetrol*, $C_{54}H_{46}O_{20}$, which forms greenish-blue masses.

Dimethylprotocetraric acid, $C_{54}H_{40}O_{25}(OMe)_2$, obtained by boiling fumaroprotocetraric acid with potassium hydrogen carbonate and methyl alcohol in a reflux apparatus, forms small, yellow prisms, commences to decompose at 40°, and is blackened without melting at 260°; it dissolves in concentrated sulphuric acid to a yellow solution which changes to blood-red. The potassium salt crystallises in small, colourless prisms.

Triethylprotocetraric acid, $C_{54}H_{39}O_{24}(OEt)_3$, is identical with cetraric acid; the potassium salt, $C_{54}H_{36}O_{24}(OEt)_3K_3$, crystallises in small, white needles.

Diethylprotocetraric acid, $C_{54}H_{40}O_{25}(OEt)_2$, obtained from fumaroprotocetraric acid, crystallises in stellate groups of white needles, and is completely decomposed, without having melted, at 250°; the potassium salt, $C_{54}H_{37}O_{25}(OEt)_2K_3$, crystallises in white needles. *Diethylcetrol*, $C_{51}H_{38}O_{18}(OEt)_2$, separates from water as an amorphous, flocculent precipitate, and sinters and decomposes at 250°.

Bisdiethylcetrol, $(C_{55}H_{48}O_{20})_2$, formed along with diethylcetrol by the action of alcoholic sulphuric acid on fumaroprotocetraric acid, is a dark blue substance, which, when heated to high temperatures, burns without previous melting, and dissolves in aqueous sodium hydroxide to a yellow solution.

The acid previously obtained from *Parmelia saxatilis* var. *sulcata* and *panniformis* (Abstr., 1901, i, 151), and termed protocetraric acid, neither yields fumaric acid when sublimed nor alkylcetrols when heated with alcoholic sulphuric acid; it is to be distinguished as parmatic acid. Contrary to Zopf's statement (Abstr., 1901, i, 87), *Parmelia Borreri* contains atranorin as well as lecanoric acid.

Parmelia tinctorum, from Madras cinchona bark, yields lecanoric acid and atranorin.

P. perlata contains atranorin and *perlatic acid*, $C_{27}H_{27}O_9 \cdot OMe,2H_2O$, which crystallises in small, white needles, loses $2H_2O$ at 80°, melts, when slowly heated, at 100—105°, when quickly heated, at 125—130°, gives a red coloration with bleaching powder in alcoholic solution, a dark blue coloration with ferric chloride, and dissolves in concentrated sulphuric acid to a colourless solution, which becomes greenish-brown on warming. The *potassium* salt, $C_{28}H_{29}O_{10}K,2H_2O$, crystallises

in white prisms; the *barium*, *copper*, $(C_{28}H_{29}O_{10})_2Cu$, *silver*, $C_{28}H_{29}O_{10}Ag$, and the basic *lead*, $5(C_{28}H_{29}O_{10})_2Pb,PbO$, are described. The *ethyl* ester, $C_{27}H_{29}O_8\cdot CO_2Et$, is obtained as a colourless, strongly refractive oil, which slowly solidifies to white needles, melts at 56—58°, and with bleaching powder in alcoholic solution gives an intensely red, with ferric chloride a dark blue, coloration.

When warmed at 85° with acetic anhydride, anhydrous perlatic acid yields *diacetylperlatide*, $C_{28}H_{26}O_9Ac_2$, which forms a white powder and melts at 55°. When boiled with aqueous baryta, perlatic acid forms barium carbonate and *perlatol*, $C_{27}H_{30}O_8$, which sinters at 60° and melts at 80°.

Along with perlatic acid there occurs in *P. perlata* an acid which crystallises in small, white needles, melts at a little above 100°, gives a bluish-violet coloration with ferric chloride, red with bleaching powder in alcoholic solution, and forms an amorphous *potassium* salt.

P. caperata, from a sandstone wall, from *Castanea vesca* near Neu Schloss in Baden-Baden, and from beech trees in the neighbourhood of Solitude, near Stuttgart, yields *d*-usnic, capraric, and caperatic acids.

Sticta pulmonaria contains stictaic acid (stictinic acid, Knop and Schnedermann, *J. pr. Chem.*, 1846, **39**, 365), and not protocetraric acid as previously stated (Abstr., 1898, i, 681).

Stictaic acid, $C_{18}H_{11}O_8\cdot OMe$, crystallises in small, yellow needles containing 2—6 per cent. of water of crystallisation lost at 100°, melts and decomposes at 264°, gives a purple coloration with ferric chloride in alcoholic solution, and dissolves in sulphuric acid to an orange-coloured solution. The *potassium*, $C_{19}H_{13}O_9K$, and the *barium*, $(C_{19}H_{13}O_9)_2Ba$, salts have been analysed.

Aspicilia gibbosa yields *aspicilic acid*, which crystallises in colourless, flat needles, melts at 119°, and, with barium chloride in ammoniacal solution, gives (1) a white, flocculent precipitate *aspicilin*, which crystallises in long, colourless, glistening leaflets, melts at 150°, distils without decomposition, and dissolves in concentrated sulphuric acid to a colourless solution which becomes brown when heated, and (2) a small amount of an acid which gives a blue coloration with ferric chloride.

Traces of atranorin are now found along with lecanoric acid in *Urceolaria scruposa* var. *vulgaris*. *Sodium lecanorate*, $C_{16}H_{13}O_7Na,4H_2O$, crystallises in small, white needles.

Chiodecton sanguineum (*C. rubrocinctum*), from Bolivian calisaya bark, contains *chiodectonic acid*, $C_{14}H_{18}O_5$, which forms a scarlet, flocculent precipitate, dissolves in alcohol to a blood-red solution, decolorised by bleaching powder, and gives a black coloration with ferric chloride, and *chiodectin*, which crystallises in long needles, melts at 120°, and is neutral.

Contrary to the statements of previous authors, *Pertusaria dealbata* does not contain orcin. G. Y.

Some Archil Lichens and their Chromogens. OSWALD HESSE (*Ber.*, 1904, **37**, 4693—4696. Compare Abstr., 1898, i, 531).—Contrary to Ronceray's statements (Abstr., 1904, i, 897), erythrin (erythric acid) melts at 148° (see *loc. cit.*, and Juillard, Abstr., 1904, i, 593), and lecanoric acid at 166°; the Maquenne block is evidently not

suitable for these substances. Erythrin is found in *Roccella Montagnei*, *R. fuciformis*, and *R. fructicosa* (*R. cacticola*; *R. peruensis*), but not in *R. tinctoria*, which contains lecanoric acid. Ronceray's supposed *Dendrographa leucophaea* was *R. fructicosa*.

Erythrin is not obtained from any *Pertusaria*; Ronceray's erythrin was probably lecanoric acid.

The vanillin-sulphuric acid test is not trustworthy for orcinol in the lichens.

Juillard's anhydroerythric acid and "simple erythrin" (*loc. cit.*) were impure erythric acid, to which the author assigns the formula $C_4H_6(OH)_3 \cdot O \cdot C_6H_2Me(OH) \cdot CO \cdot O \cdot C_6H_2Me(OH) \cdot CO_2H$; picroerythric acid then becomes $C_4H_6(OH)_3 \cdot O \cdot C_6H_2Me(OH) \cdot CO_2H$. G. Y.

[Sulphonic Acids of Benzaldehyde.] Chemische Fabrik vorm Sandoz (D.R.-P. 154528).—On dissolving toluenesulphonic acids in fuming sulphuric acid and adding manganese dioxide, oxidation to the corresponding benzaldehyde-sulphonic acids takes place, the aldehydic group remaining unattacked, even when a large excess of oxidising agent is employed. Sulphur trioxide is added from time to time to take up the water formed; the product is then poured on to ice and separated by means of sodium hydrogen sulphite. The sodium salts of benzaldehyde-*p*-sulphonic and benzaldehyde-2 : 4-disulphonic acids are described. The salts yield white and yellow phenylhydrazones respectively, and the latter gives rise to the disulphonated leuco-base of malachite green when condensed with dimethyl- or diethyl-aniline.

C. H. D.

Preparation of Aromatic Dihydroxyaldehydes. Rudolf Sommer (D.R.-P. 155731).—Hydrogen peroxide oxidises aromatic monohydroxyaldehydes in the presence of ferrous sulphate to dihydroxyaldehydes. After removing the iron by means of barium hydroxide, the aldehyde is precipitated by lead acetate. The new hydroxyl group takes the ortho-position to that already present, the aldehydic group not being attacked. Thus *m*- and *p*-hydroxybenzaldehydes yield protocatechualdehyde, and salicylaldehyde yields 2 : 3-dihydroxybenzaldehyde, together with a small quantity of resorcylaldehyde (compare Fenton and Jones, Trans., 1900, **77**, 69; Cross, Bevan, and Heiberg, Abstr., 1900, i, 534). C. H. D.

Cyclic Compounds. Oxidation of 2-Methyl*cyclo*hexanone. Wladimir B. Markownikoff (*Annalen*, 1904, **336**, 299—309. Compare Abstr., 1903, i, 836).—The product of the oxidation of 2-methyl*cyclo*hexanone contains, in addition to the three acids previously mentioned (*loc. cit.*), an acid which is very soluble in water and melts at a lower temperature than does pyrotartaric acid. Bouveault and Tétry's dianilide method of separating β- and α-methyladipic acids (Abstr., 1901, i, 364) is unsatisfactory, as, contrary to these authors' statement (*loc. cit.*), α-methyladipic dianilide, which melts at 174—175°, is slightly more soluble in alcohol than is the β-dianilide.

The pyrotartaric acid formed in the oxidation probably becomes inactive during the distillation, as the active anhydride, which melts

at 67—67·5°, after distillation under 760 mm. pressure melted at 42—45°, and when boiled for five minutes was completely converted into the inactive anhydride. G. Y.

Action of Ammonium Sulphide on Ketones and the Conversion of Thiopinacones into Hydrocarbons. WILHELM MANCHOT and PAUL KRISCHE (*Annalen*, 1905, **337**, 170—204).—The earlier experiments of Behr, Engler, and Baumann and Fromm on the action of hydrogen sulphide or hydrosulphides on acetophenone and benzophenone is discussed. Besides repeating their experiments, the authors have investigated the reaction of ammonium sulphide on other aromatic ketones.

p-Dinitrodibenzyl ketone, prepared by nitrating dibenzyl ketone with fuming nitric acid, forms microscopic crystals melting at 105°; it is oxidised to *p*-nitrobenzoic acid by nitric acid, and gives a very delicate red coloration with alkali hydroxides. The *oxime* crystallises in needles melting at 133°, and gives a red coloration with alcoholic potassium hydroxide. The *phenylhydrazone* crystallises in needles melting at 136°. On reduction with stannous chloride, basic substances are formed, but when suspended in alcohol and treated with alcoholic ammonium sulphide containing excess of hydrogen sulphide it is converted into *p-dinitrodibenzylthioketone*, $CS(CH_2 \cdot C_6H_4 \cdot NO_2)_2$ (or the corresponding mercaptan), which crystallises in needles melting at 137°. Dibenzyl ketone is readily converted by the same reagent into tetrabenzylthiopinacone, $SH \cdot C(CH_2Ph)_2 \cdot C(CH_2Ph)_2 \cdot SH$, which crystallises in long needles melting at 117°.

The investigation of the action of ammonium hydrosulphide on alcoholic solutions of acetophenone led to results differing widely from those of Baumann and Fromm, who obtained two isomeric diphenylthiophens, melting respectively at 119° and 152°, whereas the authors obtained *diphenyldimethylthiopinacone*,

$$SH \cdot CMePh \cdot CMePh \cdot SH,$$

which forms scales melting at 118°. The substance obtained by Engler from benzophenone was found to be tetraphenylthiopinacone, and not a disulphide.

Didiphenylenethiopinacone, $C_{26}H_{18}S_2$, was prepared from diphenylene ketone (fluorenone) by treatment with alcoholic ammonium hydrosulphide, and crystallised in long needles melting at 165°.

Tetrabenzyltetramethylthiopinacone, $C_{34}H_{38}S_2$, was prepared in a similar manner from diphenylpentanone in quantitative yield; it crystallised in needles melting at 112°.

Tetrabenzylethylene, $C(CH_2Ph)_2{:}C(CH_2Ph)_2$, was obtained from the tetrabenzylthiopinacone by heating with copper powder, and fractionating the oily product, which boiled at 304°, had a faint violet fluorescence, and formed an additive product with bromine. On nitration, it yielded a tetranitrotetrabenzylethylene, $C_{30}H_{24}O_8N_4$, which crystallised in needles melting at 156°. On heating the thiopinacone for several hours at 180°, hydrogen sulphide is evolved and tetrabenzylthiopinacone formed together with sulphur.

Tetraphenylthiopinacone is converted into tetraphenylethane when heated with copper, but when heated alone into tetraphenyl-

ethylene, which crystallises in leaflets melting at 224° and does not yield a picrate, but forms a tetrabromo-derivative (m. p. 253°).

Didiphenylenethiopinacone is converted into didiphenylene-ethane (m. p. 249°) on boiling its alcoholic solution with copper powder; if the pinacone is heated directly with copper, a very small quantity of a substance crystallising in brownish-red needles and melting at 203° is obtained together with *diphenylene-ethylene*, $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}>C:CH_2$; the latter forms orange-red crystals with an aromatic odour which melt at 104—106°. When heated alone at 300°, this pinacone decomposes, hydrogen sulphide being evolved, and a hydrocarbon (diphenylene-ethylene?) melting at 106° formed. Since it was possible that the formation of diphenylene-ethylene was due to the decomposition of didiphenylene-ethane, the latter was heated with copper; a small quantity of diphenylene-ethylene was produced. Since Graebe obtained didiphenylene-ethylene by distilling fluorene with lead oxide, it was probable that lead oxide could be used to remove the sulphur from didiphenylenethiopinacone, and that it would also lead to the formation of diphenylene-ethylene; such was found to be the case. Further, on heating fluorene with lead oxide, it was converted to a very large extent into diphenylene-ethylene. The diphenylene-ethylene from various sources yielded the same dibromide, $C_{14}H_{10}Br_2$, which crystallised in needles melting at 158°. When distilled with nickel in a current of hydrogen, the hydrocarbon is converted into fluorene.

K. J. P. O.

Certain Reactions of Benzoin. J. BERT. GARNER (*Amer. Chem. J.*, 1904, **32**, 583—606).—The reaction between benzoin and alcoholic potassium hydroxide or sodium ethoxide has been studied by Zinin (*J. pr. Chem.*, 1867, **98**, 495), Jena and Limpricht (*Annalen*, 1870, **155**, 93), Limpricht and Schwanert (Abstr., 1871, 536), Japp and Owens (Trans., 1885, **47**, 90), and others.

Päpcke (Abstr., 1888, 701) found that when a solution of sodium ethoxide was added to a solution of benzoin in boiling alcohol, a mass of blue crystals was produced, which became colourless when heated, but on shaking in contact with air again became coloured. On repeating this experiment, it has been found that a substance, $C_{42}H_{32}O_5Na_2$, is produced which crystallises in long, white, silky needles and is decomposed by water and most other solvents. When this compound is treated with water at 20°, benzoin, sodium hydroxide, and benzoic acid are produced. The substance is also decomposed by glacial acetic acid with formation of benzoin, benzoic acid, and sodium acetate.

On heating benzoin with alcoholic potassium hydroxide in a sealed tube for 6 hours at 150—160°, the following substances were obtained, the quantities stated being those produced from 16 grams of benzoin. Ethylbenzoin, 1·75 grams; hydrobenzoin, *iso*hydrobenzoin, and their dimolecular anhydrides, 4·9 grams; benzyl alcohol, 1·9 grams; benzoic acid, 2·2 grams; benzilic acid, 0·1 gram; and ethylbenzilic acid, 4·2 grams. The last substance resembled the ethylbenzilic acid of Jena and Limpricht (*loc. cit.*), but when heated to 70° suffered violent

decomposition with evolution of carbon dioxide and formation of a dark red, viscous oil.

In another experiment, an alcoholic solution of benzoin was heated with sodium ethoxide for 26 hours in a reflux apparatus. The products obtained from 15 grams of benzoin were as follows: hydrobenzoin, 4·2 grams; *iso*hydrobenzoin, 2·2 grams; dimolecular anhydride of hydrobenzoin, 0·8 gram; dimolecular anhydride of *iso*hydrobenzoin, 0·5 gram; benzoic acid, 2·2 grams; Jena and Limpricht's so-called ethylbenzilic acid, 4·9 grams; benzilic acid, a trace; and a tetrahydrofuran derivative, 1·9 grams.

When dry oxygen is passed into a boiling alcoholic solution of benzoin and sodium ethoxide, benzaldehyde, benzoic acid, the tetrahydrofuran derivative, and traces of benzilic acid are produced.

These experiments have shown that Jena and Limpricht's so-called ethylbenzoin is a mixture of hydrobenzoin, *iso*hydrobenzoin, and their dimolecular anhydrides; that the *iso*desoxybenzoin pinacone described by the same authors is a mixture of ethylbenzoin, *iso*hydrobenzoin, and its dimolecular anhydride; that the so-called ethyldibenzoin obtained by Jena and Limpricht, Limpricht and Schwanert, and Japp and Owens is 2-benzoyl-2 : 3-diphenyl-5-hydroxytetrahydrofuran; and that the substance to which Jena and Limpricht assigned the formula $C_{28}H_{24}O$ is impure *iso*hydrobenzoin dimolecular anhydride.

5-*Hydroxy*-2-*benzoyl*-2 : 3-*diphenyltetrahydrofuran*,

$$\begin{matrix} CH_2\cdot CH(OH) \\ | \\ CHPh\cdot CPhBz \end{matrix}\!\!>\!O,$$

crystallises from hot ethyl alcohol in large, prismatic crystals, melts at 195°, and is soluble in hot benzene, ether, acetic acid, or chloroform, gives a deep red coloration with ferric chloride, and when fused with potassium hydroxide is converted into benzoic, cinnamic, and acetic acids; its *acetyl* derivative forms large, transparent plates and melts at 145°. The tetrahydrofuran compound is oxidised by chromic acid with formation of benzoic acid and carbon dioxide; it is converted by an alcoholic solution of hydrogen chloride into ethyl cinnamate and benzil. On oxidising the compound with alkaline permanganate or with nitric acid, *γ-benzoyl-βγ-diphenylbutyrolactone* is produced, which crystallises from ethyl alcohol, melts at 138·5°, and is soluble in ethyl acetate, benzene, or chloroform.

5-Hydroxy-2-benzoyl-2 : 3-diphenyltetrahydrofuran can also be prepared by the action of cinnamaldehyde on benzoin in presence of dilute sodium ethoxide, another substance being simultaneously produced which crystallises in needles and melts at 160—161°. E. G.

o-Benzoquinone. RICHARD WILLSTÄTTER and ADOLF PFANNENSTIEL (*Ber.*, 1904, **37**, 4744—4746).—*o*-Benzoquinone, $C_6H_4O_2$, is easily obtained by oxidising catechol at the ordinary temperature with freshly prepared, purified silver oxide in pure dry ether containing ignited sodium sulphate; it crystallises in dark red, transparent plates, decomposes between 60° and 70°, has no smell, and is not volatile. On reduction with sulphurous acid, catechol is at once regenerated.

W. A. D.

Action of Azoimide on *p*-Benzoquinone. RICHARD ESCALES (*Chem. Zeit.*, 1905, **29**, 31).—By the action of azoimide on *p*-benzoquinone, a *substance* is obtained which melts at 148—153°; when crystallised from ethyl acetate, the melting point is about 25° lower.

A. McK.

Preparation of Methylaminoanthraquinones. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 156056).—Amino-derivatives of anthraquinone react with formaldehyde in strong mineral acid solution to form methylamino-derivatives. The substances may be dissolved in concentrated sulphuric acid and warmed to 55—60°. The preparation of α-methylaminoanthraquinone and of 1 : 6- and 1 : 9-dimethyldiaminoanthraquinones is described (compare Abstr., 1901, i, 839)

C. H. D.

Constitution of Dibromo-1:6-diaminoanthraquinone. ROLAND SCHOLL and A. KRIEGER (*Ber.*, 1904, **37**, 4681—4686).—Scholl and Berblinger's dibromo-1 : 6-diaminoanthraquinone (this vol., i, 88) must be the 2 : 7-dibromo-compound, as the dibromotetraminoanthraquinone obtained on reduction of Scholl's dibromodinitro-1 : 6-dinitroamino-anthraquinone (this vol., i, 70) does not react with phenanthraquinone, and therefore cannot have amino-groups in the ortho-position to each other.

2 : 7-Dibromo-4 : 9-dinitro-1 : 6-dinitroaminoanthraquinone is best prepared from crude 2 : 7-dibromo-1 : 6-diaminoanthraquinone, and is purified by treatment with alcohol and hydrogen chloride, and re-crystallisation from dilute ammonia.

2 : 7-*Dibromo*-1 : 4 : 6 : 9-*tetraminoanthraquinone*,

$$\begin{array}{l} CH:C(NH_2)\cdot C\cdot CO\cdot C\cdot C(NH_2):CBr \\ CBr:C(NH_2)\cdot C\cdot CO\cdot C\cdot C(NH_2):CBr \end{array},$$

is obtained by reduction of 2 : 7-dibromo-4 : 9-dinitro-1 : 6-diamino-anthraquinone with aqueous potassium sulphide, or of the ammonium salt of the dinitroamino-compound with hydrogen sulphide or phenyl-hydrazine in aqueous solution. It crystallises in violet, glistening needles, does not melt at 360°, is insoluble in solvents of low, but sparingly soluble in those of high, boiling point, dissolves in concentrated sulphuric acid to a brown solution, which becomes red, and finally blue on dilution, and forms a *tetrabenzoyl* derivative, $C_{42}H_{26}O_6N_4Br_2$.

G. Y.

Action of Aromatic Bases on the Nitroamino-groups of 2:7-Dibromo-4:9-dinitro-1:6-dinitroaminoanthraquinone. ROLAND SCHOLL and A. KRIEGER (*Ber.*, 1904, **37**, 4686—4692. See foregoing abstract).—When boiled with aniline, 2 : 7-dibromo-4 : 9-dinitro-1 : 6-dinitroaminoanthraquinone yields azophenine and 2 : 7-*dibromo*-1 : 6-*diamino*-4 : 9-*dianilinoanthraquinone*,

$$\begin{array}{l} CH:C(NHPh)\cdot C\cdot CO\cdot C\cdot C(NH_2){=}CBr \\ CBr:C(NH_2){-}C\cdot CO\cdot C\cdot C(NHPh):CH \end{array},$$

which crystallises from nitrobenzene in blue needles, dissolves in cold, concentrated sulphuric acid to a violet-blue solution, and, when

warmed with sulphuric acid, forms a *sulphonic acid*, which dissolves in water and dyes wool a greenish-blue colour. When heated with aniline on the water-bath, the dinitroamine yields 2 : 7-*dibromo-4 : 9-dianilinoanthraquinone*-1 : 6-*bisdiazoaminobenzene*,

$$\begin{array}{l} CH{:}C(NHPh){-}C{\cdot}CO{\cdot}C{\cdot}C(N_3HPh){:}CBr \\ CBr{:}C(N_3HPh){\cdot}C{\cdot}CO{\cdot}C{\cdot}C(NHPh){=}CH \end{array},$$

which forms a bluish-green powder, melts on the boiling water-bath, and resolidifies to a violet, glistening mass, unmelted at 300°, and aminoazobenzene.

2 : 4-*Dibromo*-1 : 6-*diamino*-4 : 9-*di*-p-*toluidinoanthraquinone*, formed by the action of boiling *p*-toluidine on the ammonium salt of the dinitroamine, crystallises in microscopic, blue needles.

The action of boiling dimethylaniline on the ammonium salt of the dinitroamine, leads to the formation of 2 : 7-*dibromo*-4 : 9-*dinitroanthraquinone*-1 : 6-*bisazoxydimethylaniline*, which crystallises in blue, ball-like aggregates and yields 2 : 7-dibromo-4 : 9-dinitro-1 : 6-diamino-anthraquinone when strongly heated or when boiled with nitrobenzene. G. Y.

Sulphonic Acids of *p*-Aminohydroxyanthraquinones. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 155440).—The introduction of a *p*-hydroxy-group into α-amino- or α-alkylamino-anthraquinones by the action of fuming sulphuric acid (Abstr., 1904, i, 1032) is also applicable to the sulphonic acids of those compounds. The preparation of 1-amino-4-hydroxy-7-sulphonic acid and its *methyl* and *ethyl* derivatives is described. C. H. D.

A New α-Sulphonic Acid of Purpurin. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 155045).—Anthraquinone-α-sulphonic acid (Abstr., 1904, i, 513) is converted by fuming sulphuric acid into a new *purpurin-α-*(6- or 9-)*sulphonic acid*. A sulphuric ester is first formed, and may be salted out by means of potassium chloride, and this intermediate product is then hydrolysed to purpurin-α-sulphonic acid by dissolving in hot potassium hydroxide, acidifying with hydrochloric acid, and boiling. The alkali salts are red in colour. C. H. D.

[A New Purpurinsulphonic Acid.] Badische Anilin- & Soda-Fabrik (D.R.-P. 154337).—Anthraquinone-β-sulphonic acid is converted by concentrated sulphuric acid containing a mercury salt and arsenic or phosphoric and nitrous acids into a new *purpurinsulphonic acid*, which differs from the products obtained by direct sulphonation of purpurin. The acid dissolves in water to a red solution, from which it is precipitated by mineral acids; the alkaline solutions are red. Soluble dyes, containing the sulphonic acid group, are obtained on heating the acid with aromatic amines at 120—190°, with or without the addition of condensing agents. The products are mixtures of compounds containing one and two amine residues. C. H. D.

Dialkyl Ethers of Anthrachrysone Derivatives. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 155633. Compare Abstr., 1903, i, 840).—The nitro- and halogen derivatives of anthra-

chrysone react with methyl sulphate to form ethers, only two methyl groups being introduced.

Dinitroanthrachrysone dimethyl ether is a yellow, crystalline powder, insoluble in most solvents and melting above 300°. *Diaminoanthrachrysone dimethyl ether,* obtained by reduction of the dinitro-compound, is blue in colour.

Tetrabromoanthrachrysone, prepared by the addition of bromine in excess to an aqueous solution of anthrachrysonedisulphonic acid, is an insoluble, orange powder; the *dimethyl ether* forms an insoluble, orange, crystalline powder. C. H. D.

α-Derivatives of Geraniol. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 154656. Compare Abstr., 1904, i, 842).—The compounds obtained from citral and magnesium alkyl or aryl haloids may be decomposed by means of concentrated organic acids instead of dilute mineral acids. The preparation of α-methyl- and α-ethyl-geraniols is described. C. H. D.

Terpenes and Ethereal Oils. LXX. Compounds of the Thujone Series. OTTO WALLACH (*Annalen*, 1904, **336**, 247—280. Compare Abstr., 1893, i, 105; 1895, i, 619; 1897, i, 246; 1902, i, 801; 1903, i, 103; 1904, i, 104).—[With E. BÖCKER.]—Thujone is obtained in two chemically identical, but physically isomeric, modifications, which are best obtained in a state of purity by conversion into their semicarbazones and hydrolysis of these by means of phthalic anhydride.

α-Thujone has $[\alpha]_D - 10\cdot23°$; it forms a lævorotatory, oily oxime and two semicarbazones, the one of which crystallises in rhombic prisms $[a:b:c = 0\cdot7157:1:0\cdot4895]$, melts at 186—188°, has $[\alpha]_D + 59\cdot5°$, and is only slightly soluble in cold ether or methyl alcohol; the other semicarbazone is amorphous, melts at about 110°, and has $[\alpha]_D$ approximately the same as the crystalline modification, than which it is more easily hydrolysed. α-Thujone is partially converted into the β-modification by warm alcoholic potassium hydroxide; it is transformed completely into β-thujone, and afterwards into *iso*thujone by alcoholic sulphuric acid.

β-Thujone has $[\alpha]_D + 76\cdot16°$; it forms a crystalline oxime which melts at 54—55° and has $[\alpha]_D + 105\cdot1°$, and a dimorphous semicarbazone which has $[\alpha]_D + 215\cdot76°$ to $+221\cdot47°$; the hexagonal modification $[a:c = 1:4\cdot063]$, obtained on rapid cooling of the methyl-alcoholic solution, melts at 174—175°, and in solution at the ordinary temperature gradually changes into the stable modification, which crystallises in rhombic prisms $[a:b:c = 0\cdot252:1:0\cdot705]$, melts at 170—172°, has a sp. gr. 1·11 at 25°, and is more easily soluble in methyl alcohol than the crystalline semicarbazone of α-thujone.

Both α- and β-thujones yield α-thujaketonic acid, which has $[\alpha]_D + 191\cdot99°$ when oxidised with potassium permanganate. At certain temperatures and concentrations, solutions of the semicarbazones of α- and β-thujones deposit mixed crystals of varying melting points, especially a form which crystallises in needles and melts at 150—152°.

As β-thujone also is converted into a mixture of α- and β-thujones when warmed with alcoholic potassium hydroxide, these two modifica-

tions differ only in regard to the asymmetric carbon atom to which the methyl group is attached, and the conversion of one into the other takes place owing to momentary formation of the enol-form, $CH_2<\overset{CH-CMe}{\underset{CPr^{\beta}\cdot CH_2}{|}}>C\cdot OH$, under the influence of the alkali hydroxide.

Oil of thuja contains principally α-thujone, oil of tansy principally β-thujone, in each case with traces of the other modification; oil of absinth contains β-thujone with smaller quantities of the α-form, whilst the oils of sage and of *Artemisia Barrelieri* contain the two modifications in about equal amounts.

[With W. Fritzsche.]—The oxime of β-thujone, when treated with benzoyl chloride according to the Schotten-Baumann method, yields a *benzoyl* derivative which separates from methyl alcohol in colourless crystals and melts at 52—53°. The action of phosphorus pentachloride on the oxime in chloroform solution leads to the formation of the *iso*oxime, which melts at 90°, boils at 155—175° under 11 mm. pressure, and is reduced by sodium and alcohol to the secondary base, $C_{10}H_{19}N$. This forms a *nitrosoamine*, $C_{10}H_{18}N\cdot NO$, which melts at 55—56°. The *platinichloride* of the base, $(C_{10}H_{18}NMe_2Cl)_2PtCl_4$, was analysed.

When acted on by benzoyl chloride in alkaline solution, the oxime of *iso*thujone yields a *benzoyl* derivative, $C_{10}H_{16}ONBz$, which crystallises in needles and melts at 139—140°. With hydrogen chloride in ethereal solution, *iso*thujoneoxime forms the crystalline hydrochloride, $C_{10}H_{17}ON,HCl$. *iso*Thujoneamine, obtained by reduction of the oxime, forms a *benzoyl* derivative, $C_{10}H_{18}NBz$, which melts at 127—128°. When reduced with sodium in alcoholic solution, the oxime yields 56 per cent. of *iso*thujoneamine, the remainder being converted into *iso*thujone with evolution of ammonia.

The *benzoyl* derivative of thujamenthone, $C_{10}H_{18}ONBz$, melts and decomposes at 135—136°. The liquid product obtained in the thujamenthone oxime is now shown to be a mixture of the oxime with the *iso*oxime. When oxidised with potassium permanganate in warm aqueous solution, the *iso*oxime yields hydroxythujamenthone *iso*oxime, $\begin{array}{l}CHPr^{\beta}\cdot CHMe\cdot CMe\cdot OH \\ | \qquad\qquad\qquad\quad | \\ CH_2 —— CO —— NH\end{array}$, which melts at 173—174°, and *iso*propyllævulic acid. When the hydroxy*iso*oxime is boiled with 20 per cent. hydrochloric acid, it is converted into thujamenthoketonic acid.

G. Y.

Essential Oil of the Wood of Thuja Articulata of Algeria. Emilien Grimal (*Compt. rend.*, 1904, **139**, 927—928).—The essential oil of the wood of *Thuja articulata* contains carvacrol, thymoquinol, and thymoquinone.

N. H. J. M.

Condensation Product from Hæmatoxylin and Formaldehyde. Roberto Lepetit (D.R.-P. 155630).—Hæmatoxylin condenses with formaldehyde on heating with acids at 100°, or without acids at 110—115° under pressure. The product is an insoluble, brownish-red powder with metallic lustre, and dissolves readily in dilute alkalis to a bluish-red solution, or in alcohol, acetic acid,

glycerol, or acetone to dark brownish-red solutions. It is tasteless and non-poisonous and possesses astringent properties. C. H. D.

Dyes of the Cyanine Series. Aktien-Gesellschaft für Anilin-Fabrikation (D.R.-P. 155541).—The alkyl haloid compounds of methylated quinolines are oxidised in alkaline solution by potassium ferricyanide or potassium persulphate, forming dyes of the cyanine series. No similar dye is obtained from quinoline alkyl iodides, the presence of a methyl group in the quinoline ring being essential. The products dissolve in alcohol to blue solutions, and may be employed to increase the sensibility of photographic plates. The absorption-spectra of the dyes from quinaldine, lepidine, *p*-toluquinaldine, and a mixture of the latter with *p*-toluquinoline are described. C. H. D.

[Formation of Furoyl Derivatives by means of Pyromucic Chloride.] Erich Baum (*Ber.*, 1904, **37**, 4756).—A correction (compare Abstr., 1904, i, 910). W. A. D.

Halogen Derivatives of Fluoran. Badische Anilin- & Soda-Fabrik (D.R.-P. 156333).—Dichlorofluoran may be readily prepared by heating phthalic anhydride and *m*-chlorophenol with zinc chloride. Condensation then occurs with the formation of a pyrone ring. The reaction is also applicable to the homologues of *m*-chlorophenol or *m*-bromophenol and to the halogen derivatives of phthalic anhydride.

o-*Chloro*-p-*cresol* (2-*chloro*-4-*hydroxytoluene*), prepared by boiling the diazonium compound of 2-chloro-*p*-toluidine, forms colourless needles melting at 55°, and boils at 228°; it dissolves very readily in alcohol or ether, and separates from water in spear-like crystals. o-*Bromo*-p-*cresol* melts at 55—56°, boils at 245—246°, and dissolves sparingly in water. 3 : 4-*Dichlorophenol* forms colourless needles; it melts at 64—65° and boils at 145—146°.

Tetrachlorofluoran, from dichlorophenol and phthalic anhydride, melts at 255°; *dichlorodimethylfluoran* forms small, colourless crystals and melts at 285°; *dibromodimethylfluoran* melts at 284—285°.

C. H. D.

Ethylacetylacetone and its Condensation Products with Polyvalent Phenols. Carl Bülow and Ivo Deiglmayr (*Ber.*, 1904, **37**, 4528—4531. Compare Bülow, Abstr., 1903, i, 272; Bülow and Deiglmayr, Abstr., 1904, i, 609).—When hydrogen chloride is passed into a solution of methylacetylacetone and resorcinol in glacial acetic acid containing a little acetic anhydride, ether being added when the dark brown mass becomes viscous, glistening, greenish-yellow crystals of the *hydrochloride* of 7-*hydroxy*-2-*methyl*-3-*ethyl*-4-*methylene*-1 : 4-*benzopyran*, $\begin{matrix} OH\cdot C{=}CH\cdot C\cdot O(HCl)\cdot CMe \\ CH{:}CH\cdot C\cdot C({:}CH_2)\cdot CEt \end{matrix}$, separate. The *picrate*, prepared by adding picric acid to a boiling alcoholic solution of the hydrochloride, crystallises in yellow needles and dissolves in concentrated sulphuric acid to a yellow solution with slight blue fluorescence.

The constitution of 7-hydroxy-2-methyl-3-ethyl-4-methylene-1 : 4-

benzopyran was proved by the isolation of methyl propyl ketone, resacetophenone, and acetic acid from the products of the action of potassium hydroxide on the hydrochloride. C. H. D.

Three Position Isomeric Hydroxyl Derivatives of Resacetein. Carl Bülow and Constant. Sautermeister (*Ber.*, 1904, **37**, 4715—4723. Compare Abstr., 1904, i, 262, 609, 610).—The *hydrochloride* of 5 : 7-*dihydroxy*-2-op-*diethoxyphenyl*-4-*methylene*-1 : 4-*benzopyran*,

$$C_6H_2(OH)_2<\overset{\text{———O———}}{C(:CH_2)\cdot CH}>C\cdot C_6H_3(OEt)_2,$$

is obtained by the condensation of diethoxybenzoylacetone with phloroglucinol in acetic acid solution, and in presence of hydrogen chloride at 30—40°. It crystallises from a mixture of alcohol, water, and concentrated hydrochloric acid in anhydrous, orange-red needles, which are hydrolysed to the base when boiled with water. The *picrate*, $C_{26}H_{23}O_{12}N_3$, crystallises in orange-red needles, is sparingly soluble, begins to melt at 216°, and is completely decomposed at 225°. The *platinichloride*, $(C_{20}H_{20}O_5)_2,H_2PtCl_6$, forms a yellowish-brown, crystalline precipitate, and the *base* itself crystallises from alcohol in small, dark reddish-brown needles, which melt and decompose at 170—180°. Its solution in concentrated sulphuric acid exhibits a feeble green fluorescence.

An isomeric 7 : 8-*dihydroxy*-derivative is obtained by the condensation of diethoxybenzoylacetone with pyrogallol; it crystallises in violet-black, glistening needles containing $1H_2O$, is moderately soluble in most organic solvents, and melts and decomposes at 196—201°. The *hydrochloride* crystallises in dark red needles, the *sulphate*, $C_{20}H_{20}O_5,H_2SO_4$, forms dark red, glistening needles melting at 236—242°, and its solution in concentrated sulphuric acid does not fluoresce. The *picrate* decomposes at about 215°, and the *diacetyl* derivative, $C_{24}H_{24}O_7$, crystallises in orange-red plates, very sparingly soluble in the usual solvents.

The 6 : 7-*dihydroxy*-derivative, obtained from hydroxyquinol, crystallises from alcohol in garnet-red, quadratic plates with a blue lustre, melts and decomposes at 198—211°, is readily soluble in most organic solvents, and its solution in concentrated sulphuric acid exhibits a deep green fluorescence. The *hydrochloride* crystallises in golden-yellow, glistening needles containing $1{\cdot}5H_2O$. The *picrate* also forms golden-yellow crystals which melt and decompose at 195—208°. The *sulphate* forms glistening, brown needles which melt at 204—214°, and the *diacetyl* derivative forms dark red, glistening needles melting at 235—250°. Its solution in sulphuric acid does not fluoresce.

The dyeing properties of the 5 : 7- and 7 : 8-dihydroxy-compounds have been tested. J. J. S.

Influence of Alkaloids on Certain Processes of Oxidation. E. Feder (*Arch. Pharm.*, 1904, **242**, 680—704).—It is known that certain metallic salts (namely, copper sulphate, mercuric chloride, silver nitrate, ferric chloride, gold chloride, and platinum chloride) are able to oxidise the solutions of certain organic substances (namely, guaiacum resin or guaiaconic acid, aloin, indigocarmin, pyrogallol, catechol,

quinol, orcinol) with production of a coloration. This action, often slow in itself, is frequently much accelerated by the presence of an alkaloid. The influence of many alkaloids in this direction has been investigated; for details, the original paper must be consulted.

The influence of alkaloids on the reduction of copper salts by dextrose and on the biuret reaction has also been examined.

C. F. B.

A New Series of Bases derived from Dihydroberberine. MARTIN FREUND and HEINRICH BECK (*Ber.*, 1904, **37**, 4673—4679. Compare Abstr., 1904, i, 915).—In addition to berberinal, the salts of berberine also react with magnesium alkyl or aryl haloids yielding α-derivatives of dihydroberberine. α-Benzyldihydroberberine forms a *hydrochloride*, $C_{27}H_{25}O_4N,HCl$, crystallising from alcohol and ether and melting at 165—166°. The *methiodide* separates from alcohol as a yellow, crystalline powder and sinters at 170° and decomposes at 181—182°.

α-*Methyldihydroberberine*, from berberine hydrochloride and magnesium methyl iodide, separates from dilute alcohol in yellow crystals and melts at 134—135°. The *hydriodide* separates from dilute alcohol in bright yellow leaflets and melts at 249°; the crystalline *hydrobromide* rapidly darkens.

α-*Phenyldihydroberberine* is precipitated by ammonia from its solution in alcohol and acetic acid in brownish-yellow, glistening tablets melting at 195°.

C. H. D.

Normal Quinine Hydrochloride. CARLO ERBA (*J. Pharm. Chim.*, 1904, [vi], **20**, 550—551).—The author draws attention to his study of the subject published in the *Boll. farm.*, 1901. According to his observations, the salt crystallises from 95 per cent. alcohol, is hydrated, and has the formula $C_{20}H_{24}O_2N_2,2HCl,C_6H_6O,H_2O$, whilst Carette (Abstr., 1904, i, 1044) stated that it contained 1·5 mols. of alcohol.

G. D. L.

Constitution of β-*iso*Cinchonicine. KARL KAAS (*Monatsh.*, 1904, **25**, 1145—1152. Compare Abstr., 1900, i, 605).—β-*iso*-ψ-Cinchonicine is now found to be a keto-base like cinchonicine (compare Miller and Rohde, Abstr., 1894, i, 431, 432), and is therefore to be called β-*iso*-cinchonicine. The action of phosphorus pentachloride on β-*iso*-cinchonicine in chloroform solution leads to the formation of hydrogen chloride and the *hydrochloride* of a chloro-base, $C_{19}H_{21}N_2Cl,2HCl$, which crystallises in short, yellow prisms, melts at 150°, and is hygroscopic; the chloro-base, like cinchonine chloride, does not lose chlorine when the salt is shaken with silver acetate in glacial acetic acid solution. The *hydrochloride* of the benzoyl derivative,

$$C_{26}H_{25}O_2N_2,HCl,H_2O,$$

obtained by shaking the base with benzoyl chloride in benzene solution, crystallises in needles, melts at 228°, and is not hydrolysed when boiled with potassium hydroxide for half an hour. The action of acetic anhydride on the base leads to the formation of an oily *acetyl* derivative. When treated with methyl iodide in methyl-alcoholic

solution, *β-iso*cinchonicine forms the *hydriodide* of the methyl base, $C_{19}H_{21}ON_2Me,HI$, which crystallises in short, yellow prisms, decomposes at 268°, and when treated successively with ammoniacal methyl alcohol and hydrochloric acid is converted into the *hydrochloride.* This is also obtained by heating *β-iso*cinchonine methiodide with aqueous potassium hydroxide and treating the product with hydrochloric acid. G. Y.

Creatinine. Georg Korndörfer (*Arch. Pharm.*, 1904, **242**, 641—648).—The creatinine used was prepared from urine. When heated with methyl iodide and methyl alcohol, it formed a *methylcreatinine hydriodide*, $C_5H_9ON_3,HI$, melting at 212°; the corresponding *hydrochloride, aurichloride* melting at 174°, *platinichloride* with $\frac{1}{2}H_2O$, and *picrate* melting at 183° were also prepared. By decomposing the hydriodide with silver oxide, the base was obtained in an amorphous state. The hydrochloride, however, could be decomposed with potassium carbonate (and therefore cannot be a quaternary ammonium salt); obtained in this way, the *base* forms crystalline, hygroscopic needles of the composition $C_5H_9ON_3,H_2O$.

The base (methylcreatinine) was heated with methyl iodide and methyl alcohol, and from the product a *dimethylcreatinine platinichloride*, $2C_6H_{11}ON_3,H_2PtCl_6$, was isolated, and also a small quantity of a salt which contained a percentage of platinum approaching that in a *trimethylcreatinine platinichloride*, $2C_7H_{13}ON_3,H_2PtCl_6$.
C. F. B.

Suprarenine [Epinephrine], the Substance of the Suprarenal Glands which causes Increase of the Pressure of the Blood. E. Weyrich (*Chem. Centr.*, 1904, ii, 1575—1576; from *Verh. Ges. Deut. Naturfor. Aerzte*, 1903, ii, 127).—Suprarenine, prepared from fresh suprarenal glands of oxen by extracting with water which has been rendered faintly acid, forms a pale brown to yellow or greyish-white, sandy powder. The presence of extremely small crystals may be detected. Suprarenine is sparingly soluble in hot or cold water and is insoluble in alcohol or ether. The hydrochloric acid solution is emerald-green, but on the addition of dilute ammonia becomes carmine-red. The hydrochloride is precipitated by ammonia or alkali carbonates, but not by alkali acetates; it does not give any of the reactions of albumin, and its concentrated aqueous solution is not precipitated by alcohol. One gram of the base is sufficient to neutralise 0·195—0·2 gram of hydrogen chloride. The composition $C_{10}H_{15}O_3N,\frac{1}{2}H_2O$ is ascribed to suprarenine, and it is assumed to have a constitution similar to that of aminocatechol. E. W. W.

Skimmianine, an Alkaloid from Skimmia Japonica. J. Honda (*Chem. Centr.*, 1904, ii, 1511—1512; from *Arch. exp. Path. Pharm.*, **52**, 83—94).—A poisonous alkaloid, skimmianine, has been found to be present in all parts of *Skimmia japonica*, but most abundantly in the leaves. It was isolated from the latter by extracting with 96 per cent. alcohol. *Skimmianine*, $C_{32}H_{29}O_9N_3$, crystallises from alcohol in yellow, four-sided prisms, melts at 175·5°, and is readily soluble in chloroform or alcohol, moderately so in methyl alcohol, very

sparingly so in ether, amyl alcohol, or carbon disulphide, and insoluble in water or light petroleum. All the solutions are neutral to litmus. The solutions of the base are almost tasteless, but those of the salts are very bitter. Skimmianine is only dissolved by dilute mineral acids when present in excess, and the solutions on evaporation yield the salts which crystallise in needles. When the excess of acid is neutralised by alkali carbonates, or when the salts are dissolved in water and the solutions concentrated, the base is precipitated. Even after boiling with dilute acids, skimmianine does not reduce alkaline copper solutions. A solution of the alkaloid in hydrochloric acid gives voluminous precipitates with the ordinary alkaloid reagents, and forms a *platinichloride* which crystallises in rhombic plates, and is moderately soluble in water, but only sparingly so in alcohol. The precipitate formed with gold chloride is easily decomposed. Crystals of skimmianine dissolve in concentrated sulphuric acid forming a brownish-yellow solution, which, on the addition of potassium chlorate, becomes reddish-brown. By the action of the alkaloid on Fröhde's reagent, a green coloration is formed which afterwards becomes blue; a solution of potassium permanganate in sulphuric acid becomes violet and then yellowish-brown, and concentrated nitric acid forms a yellow solution which changes to orange-red.

Injection of skimmianine into the femoral lymphatics of *Rana esculenta* or *Rana temporaria* affects the appearance of the muscles at the place of application, and renders them stiff and brittle. The neighbouring muscles are also affected by larger doses. Voluntary motion becomes sluggish, the breathing superficial, and the pupils contract. Reflex sensibility appeared as a rule to increase only in the case of *Rana esculenta*. The absolute strength, and the work performed by the muscles, were apparently diminished. The alkaloid has probably a direct action on the muscles of the heart, decreasing the pulsations and causing disturbance of the diastole. The pulse is similarly affected even when atropine has been previously administered. Intravenous injection, in the case of rabbits, causes general symptoms of poisoning. Slight poisoning is accompanied by feeble spasms. The pressure of the blood falls even when chloral has been administered, but after a time it increases again, probably owing to the compensating contraction of the peripheral vessels. Skimmianine has no effect on the secretion of urine. E. W. W.

Pharmacological Studies on Synthetical Bases of the Piperidine Series. HERMANN HILDEBRANDT (*Zeit. physiol. Chem.*, 1904, **43**, 249—289. Compare Abstr., 1900, ii, 676, and this vol., i, 80).—Dimroth's thymolmercury chloride, $C_3H_7\cdot C_6H_2Me(OH)\cdot HgCl$ (Abstr., 1902, i, 656), does not react with formaldehyde and piperidine in the cold, but, on warming, the *methylenepiperidide* derivative, $CH{<}{\substack{C(C_3H_7)\cdot C(OH)\\ C(HgCl)=CMe}}{>}C\cdot CH_2\cdot C_5NH_{10}$, is obtained. This has very much the same physiological properties as other compounds containing mercury directly attached to the benzene nucleus.

The methylenepiperidide derivative of thymotic alcohol, melting at

141° (this vol., i, 80), is very hygroscopic, and readily yields a *platinichloride*, $(C_{17}H_{25}ON)_2PtCl_6,H_2O$, which crystallises in orange plates.

o-Thymotinpiperidide (Base 2), melting at 141°, is isomeric with *p*-thymotinpiperidide (Base 1) (Abstr., 1900, i, 676), and when taken into the animal system is eliminated as a glycuronic acid derivative, which, on hydrolysis with 8 per cent. sulphuric acid, yields the *methylated base*, $C_{17}H_{27}ON$ (Base 3), melting at 144°. This can be distinguished from Base 2 by means of its *platinichloride*, $(C_{17}H_{27}ON)_2,H_2PtCl_6$, which separates in the course of a few hours. Bases 2 and 3, but not Base 1, give characteristic thymol reactions with acetic and sulphuric acids.

p-Thymotic aldehyde and the corresponding acid and *o*-thymotic acid do not condense with piperidine and formaldehyde. When taken into the animal system, the ortho-acid is partly eliminated as such, and partly in combination with glycuronic acid. It is a much more effective poison than the para-acid, which is entirely eliminated in combination with glycuronic acid.

Dannenberg's *p*-bromothymol (Abstr., 1903, i, 338) yields a *methylenepiperidide* derivative, melting at 59°. The corresponding *o*-bromo-derivative melts at 76°. They are not poisonous, and are excreted in combination with glycuronic acid. The glycuronic acid derivatives of *o*- and *p*-thymotinpiperidides cannot be precipitated from urine by the addition of basic lead acetate, whereas the derivatives of piperidides which are physiologically inactive are readily precipitated.

Auwers and Marwedel's dibromo-*p*-hydroxy-ψ-cumyl piperidide (Abstr., 1896, i, 149) is physiologically inactive, whereas *dibromo-p-cresyl piperidide*, melting at 182°, is as active as *o*- and *p*-thymotinpiperidides.

The results of various experiments tend to show that the condensation products obtained from piperidine and phenols by means of formaldehyde exhibit an acute physiological action only when the para- or one of the ortho-positions with respect to the hydroxyl group is not substituted. The meta-position with respect to the hydroxyl has an influence on the physiological action only when both meta-positions are unsubstituted, and when the methylenepiperidine residue is adjacent. A further generalisation is that only those condensation products of piperidine with phenols and formaldehyde which have an unsubstituted ortho- or para-hydrogen atom in the benzene ring undergo methylation in the animal system; it would thus appear that it is only physiologically active compounds which undergo methylation.

The organism does not appear to be capable of introducing methyl in place of a hydrogen atom in the ortho- or para-position with respect to the hydroxyl groups, and thus forming an inactive compound, hence it is the nitrogen atom which is methylated, and the hydroxyl group reacts with the glycuronic acid, forming a compound which is physiologically inactive.

Experiments have been conducted in order to determine the effect of introducing various substituents into the piperidine ring of the condensation products.

Scholtz's *iso*-2:6-diphenylpiperidine condenses with formaldehyde and thymol when the mixture is heated, yielding a product which melts at 162°. It is physiologically inactive. 2-Methylpiperidine itself

is largely oxidised in the animal system to the corresponding carboxylic acid, which then unites with glycine.

Thymotin-2-methylpiperidide, $C_{17}H_{27}ON$, crystallises in irregular cubes, melts at 118°, and is not so physiologically active as the simple piperidide. It is eliminated in the form of a neutral derivative of glycuronic acid, which on hydrolysis yields a *methyl* derivative, $C_{18}H_{29}ON$, crystallising in needles and melting at 116°. This is much less active than the original methylpiperidide.

Carvacryl-2-methylpiperidide crystallises in needles, melts at 151°, and is extremely active. Its *platinichloride*, $(C_{17}H_{27}ON)_2,H_2PtCl_6$, crystallises readily from alcohol in flat needles. The *methylated* base, obtained by the decomposition of the excreted glycuronic acid derivative, is not so active.

Thymotin copellidide, $OH\cdot C_6H_2MePr\cdot CH_2\cdot C_5NH_8MeEt(1:4)$, melts at 115° and is still less poisonous than the 2-methylpiperidide, whereas copellidine itself is about three times as poisonous as 2-methylpiperidine.

Dibromocresyl-2-methylpiperidide is still less active. J. J. S.

Dimolecular Nitriles. ERNST VON MEYER (*J. pr. Chem.*, 1904, [ii], **70**, 560—561).—*3-Cyano-2-phenyl-6-methyl-4-pyridone*,

$$CO<\begin{matrix}C(CN):CPh\\CH_2-CMe\end{matrix}>N,$$

or *3-cyano-4-hydroxy-2-phenyl-6-methylpyridine*,

$$OH\cdot C<\begin{matrix}C(CN):CPh\\CH-CMe\end{matrix}>N,$$

is formed when a solution of benzoylacetonitrile in ethyl acetoacetate is saturated with hydrogen chloride. It crystallises in leaflets, melts at 244°, and, when heated with hydrochloric acid at 200°, yields *4-hydroxy-2-phenyl-6-methylpyridine*, which crystallises in needles and melts at 178·5°.

The action of cyanogen bromide on benzoylacetonitrile in benzene solution at 100° leads to the formation of a *bromo*-derivative,

$$CN\cdot CH_2\cdot CPh:NBr,$$

which crystallises in white needles and melts at 114°. The bromo-derivative of diacetonitrile is similarly formed by bromination with cyanogen bromide in benzene solution. G. Y.

2:6-Substituted Pyridinecarboxylic Acids. HANS MEYER (*Monatsh.*, 1904, **25**, 1196—1200. Compare Abstr., 1903, i, 364).—When warmed with methyl iodide and aqueous sodium carbonate, 6-methylpyridine-2-carboxylic acid and quinoline-2-carboxylic acid do not form the respective betaines, but after evaporation are recovered unchanged. The action of thionyl chloride on quinoline-2-carboxylic acid leads to the formation of its crystalline *chloride*, which melts and decomposes at 175—177°, and when treated with methyl alcohol yields the *methyl* ester, crystallising in matted needles melting at 78°. The *amide*, formed by the action of aqueous ammonia on the chloride or the ester, crystallises in slender, glistening needles, melts at 123°, and forms an aurichloride, which crystallises in needles and melts at 210°. The *nitrile* is formed when the amide is boiled with thionyl chloride; it crystallises in long needles, melts at 89°, is very

easily volatile, has a pleasant odour, and is more easily hydrolysed than 4-cyanoquinoline. The aurichloride crystallises in needles and melts and decomposes at 158°. G. Y.

Conversion of Tetrahydroquinoline into 2-Methyldihydroindole. JULIUS VON BRAUN and A. STEINDORFF (*Ber.*, 1904, **37**, 4723—4730).—Tetrahydroquinoline may be transformed into 2-methyldihydroindole by means of the following reactions. Benzoyltetrahydroquinoline is converted into benzoyl-*o*-γ-chloropropylanilide (Abstr., 1904, i, 918). This is stable towards quinoline, is reconverted into the tetrahydroquinoline derivative on treatment with sodium ethoxide, but when distilled under 12 mm. pressure is mainly transformed into *benzoyl*-o-*allylanilide*, $COPh\cdot NH\cdot C_6H_4\cdot CH_2\cdot CH{:}CH_2$, although benzoyl chloride and tetrahydroquinoline are formed at the same time. The benzoylallylanilide crystallises from alcohol in long needles, melts at 123—124°, and is only slowly hydrolysed by alkalis. It readily combines with hydrogen chloride when heated with three times its weight of fuming hydrochloric acid at 70—80°, yielding benzoyl-*o*-β-chloropropylanilide (this vol., i, 81).

o-β-*Chloropropylaniline*, $NH_2\cdot C_6H_4\cdot CH_2\cdot CHClMe$, is obtained when the β-chlorinated anilide or benzoyl-*o*-allylanilide itself is heated with fuming hydrochloric acid for several hours at 125°, and when heated with water it is transformed into 2-methyldihydroindole hydrochloride:

$$C_6H_4{<}{}^{CH_2\cdot CHClMe}_{NH_2} \longrightarrow C_6H_4{<}{}^{CH_2}_{NH(HCl)}{>}CHMe.$$

J. J. S.

A Method for the Preparation of Compounds derived from Pseudo-bases by the Replacement of the Hydroxyl Group by Hydrocarbon Residues. MARTIN FREUND [with EDMUND SPEYER] (*Ber.*, 1904, **37**, 4666—4672).—Such salts of organic bases as yield pseudo-bases with alkali hydroxides react with magnesium alkyl or aryl haloids, forming compounds which may be regarded as derived from the pseudo-bases by the replacement of hydroxyl by a hydrocarbon residue. The reaction is a general one.

Quinoline methiodide reacts vigorously with magnesium phenyl bromide in ethereal solution to form 2-*phenyl*-1-*methyldihydroquinoline*, $C_6H_4{<}{}^{CH=CH}_{NMe\cdot CHPh}$, which crystallises from alcohol in prisms melting at 89—90°, and dissolves readily in acetone or chloroform, but is insoluble in water. It dissolves in hydrochloric acid, and is reprecipitated on dilution. Calcium permanganate oxidises it to benzoylmethylanthranilic acid, $CO_2H\cdot C_6H_4\cdot NMe\cdot COPh$. Sodium reduces the base in alcoholic solution to 2-*phenyl*-1-*methyltetrahydroquinoline*, crystallising from alcohol in rhombic tablets melting at 106—107°, and possessing weak basic properties.

Bromine reacts with 2-phenyl-1-methyldihydroquinoline in chloroform solution, forming 3-(or 4-)*bromo*-2-*phenylquinoline methobromide*, $C_6H_4{<}{}^{CH=CBr}_{NMeBr\cdot CPh}$ or $C_6H_4{<}{}^{CBr=CH}_{NMeBr\cdot CPh}$, crystallising from water in

yellow needles and melting and decomposing at 248—250°. Sodium hydroxide precipitates the pseudo-base as an amorphous, yellow mass, dissolving readily in alcohol or ether. The *ammonium* base may be obtained by the action of moist silver oxide on the bromide, its aqueous solution may be evaporated without decomposition, and sodium hydroxide converts it into the insoluble pseudo-base.

The bromide decomposes on fusion into methyl bromide and 3-(or 4-)*bromo-2-phenylquinoline*, $C_6H_4{<}\begin{matrix}CH{:}CBr\\ N{=}CPh\end{matrix}$ or $C_6H_4{<}\begin{matrix}CBr{:}CH\\ N{=}CPh\end{matrix}$, crystallising from alcohol in white needles and melting at 120—121°.

Magnesium methyl iodide and quinoline methiodide react vigorously to form 1:2-*dimethyldihydroquinoline*, an oil becoming yellow on exposure to air and boiling at 255—256°. It dissolves readily in acids, but does not yield crystallisable salts.

Magnesium ethyl iodide and phenylacridine methiodide react to form *phenylethylmethyldihydroacridine*, $C_6H_4{<}\begin{matrix}CPhEt\\ NMe\end{matrix}{>}C_6H_4$, crystallising from alcohol or light petroleum in yellowish-white needles melting at 112° after sintering. The product has no basic properties.

C. H. D.

Hyposulphites of Aromatic Bases. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and ALPHONSE SEYEWETZ (*Bull. Soc. chim.*, 1905, [iii], **33**, 67—69).—2:4-*Diaminophenol hyposulphite*, obtained by a mixture of molecular solutions of diaminophenol hydrochloride and sodium hyposulphite in water, crystallises in white spangles and is slightly soluble in cold water (1 in 600) and alcohol. The *hyposulphites* of diaminoresorcinol and 2:4:6-triaminophenol resemble the foregoing, but that of *p*-phenylenediamine is less stable and more soluble in water. The monoamines and pyridines also yield crystalline hyposulphites.

T. A. H.

[Indophenol from *p*-Phenylenediamine and *o*-Acetylaminophenol.] KALLE & Co. (D.R.-P. 156478).—Potassium ferricyanide oxidises a mixture of *p*-phenylenediamine and *o*-acetylaminophenol, forming a blue *indophenol*. On dissolving in sodium sulphide and passing a current of carbon dioxide, the pure *leuco-indophenol* is precipitated, and may be crystallised from organic solvents. It dissolves sparingly in water, readily in acids or alkalis. The indophenol yields a blue dye on fusion with sodium sulphide and sulphur.

C. H. D.

Formation of Chains. LXV. Reactions of Di-*a*-bromo*iso*valeryldiarylethylenediamines. CARL A. BISCHOFF [and, in part, BILSEN, VON MEYSTOWICZ, PÄPKE, RADIK, ROSSI, SCHUBETSKI, TELETOFF, and WULFFIUS] (*Ber.*, 1904, **37**, 4653—4666).—Di-*a*-bromo*iso*valeryldiphenylethylenediamine, from *a*-bromo*iso*valeryl bromide and diphenylethylenediamine in presence of pyridine (compare Abstr., 1899, i, 278), is converted by sodium phenoxide or naphthoxide into *di-dimethylacrylodiphenylethylenediamine*, $C_2H_4(NPh{\cdot}CO{\cdot}CH{:}CMe_2)$, which forms

silvery needles melting at 177° and dissolving readily in chloroform, acetone, or acetic acid, less readily in alcohol or benzene.

In similar manner, di-α-bromo*iso*valeryldi-*o*-tolylethylenediamine yields *di-dimethylacryldi-*o*-tolylethylenediamine*, crystallising from alcohol in glistening needles melting at 178°. *Di-dimethylacryldi-*p*-tolylethylenediamine* crystallises from dilute alcohol in glistening needles and melts at 172°.

*Di-α-bromo*iso*valeryldi-α-naphthylethylenediamine* crystallises from ethyl oxalate in long, four-sided leaflets melting at 211—212°, and dissolves very sparingly in most organic solvents, readily in nitrobenzene. *Di-dimethylacryldi-α-naphthylethylenediamine* crystallises from glacial acetic acid in small, colourless prisms melting at 206—208°. *Di-dimethylacryldi-β-naphthylethylenediamine* separates from alcohol as sparingly soluble, silky needles melting at 187°, and dissolves readily in chloroform. C. H. D.

Diamines. ADOLF LOEWY and CARL NEUBERG (*Zeit. physiol. Chem.*, 1904, **43**, 355—357).—Diamines are usually isolated from urine either as benzoyl derivatives (von Udránszky and Baumann, Abstr., 1889, **33**, 1024) or as mercurichlorides (Brieger and Stadthagen, *Berl. Klin. Woch.*, 1889, 345). The authors employ the phenylcarbimide derivatives.

Tetramethylenediaminephenylcarbimide,

$$NHPh\cdot CO\cdot NH\cdot[CH_2]_4\cdot NH\cdot CO\cdot NHPh,$$

obtained by mixing the components in ethereal solution, crystallises from a mixture of pyridine and acetone in needles melting at 240° (corr.) and is insoluble in the ordinary solvents.

The corresponding *derivative* of *pentamethylenediamine*, $C_{19}H_{24}O_2N_4$, melts at 207—209° (corr.) and is more readily soluble in a mixture of pyridine and acetone. The *ethylenediamine* derivative melts at 263°. J. J. S.

Action of Secondary Asymmetric Hydrazines on Sugar. I. RUDOLF OFNER (*Monatsh.*, 1904, **25**, 1153—1163. Compare Abstr., 1904, i, 798, 936).—Whilst phenylmethylosazone is formed by the action of phenylmethylhydrazine on dextrose or lævulose, no osazone is formed by the action of pure *as*-phenylbenzylhydrazine on either of those substances. Neuberg's supposed lævulose-phenylbenzylosazone (Abstr., 1902, i, 264) is phenylbenzylphenylosazone, which is obtained by the action of phenylbenzylhydrazine containing phenylhydrazine on dextrose or lævulose, or of pure phenylbenzylhydrazine on phenylglucosazone. G. Y.

[Chloroindanthrene.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 155415).—A mixture of concentrated nitric acid and fuming hydrochloric acid converts indanthrene at 50° into *chloroanthraquinoneazine*, a yellow, fairly stable compound, which is reduced by sodium hyposulphite to *chloroindanthrene*, dissolving in nitrobenzene or aniline to green solutions, insoluble in water or sodium hydroxide. C. H. D.

Study and Synthetical Preparation of Aryl Thiohydantoins. M. Emmanuel Pozzi Escot (*Compt. rend.*, 1904, **139**, 1031—1032).—Disubstituted ψ-thiohydantoins, readily prepared by the action of monochloro- or monobromo-acetic acid on the *s*-arylthiocarbamides (compare Abstr., 1904, i, 869), are crystalline compounds, decomposed by alkalis yielding the corresponding *s*-arylcarbamides according to the equations:

$$RN{:}C{<}{}^{SH}_{NHR} + CH_2Cl{\cdot}CO_2H = RN{:}C{<}{}^{S-CH_2}_{NR\cdot CO},$$

$$RN{:}C{<}{}^{S-CH_2}_{NR\cdot CO} + 2H_2O = CO(NHR)_2 + HS{\cdot}CH_2{\cdot}CO_2H.$$

Di-o-*tolyl-ψ-thiohydantoin* forms slightly yellow, octahedral crystals melting 4° lower than the corresponding thiocarbamide, is slightly soluble in water and readily so in boiling alcohol or cold xylene, toluene, or chloroform. *Di*-p-*tolyl-ψ-thiohydantoin* crystallises from alcohol in almost colourless, small, square plates and melts at 115°. *Di-α-naphthyl-ψ-thiohydantoin* crystallises from alcohol in white prisms and melts at 183°; the β-isomeride possesses similar properties. Diphenyl-ψ-thiohydantoin crystallises from alcohol and melts at 174°.

M. A. W.

Action of Magnesium Benzyl Chloride on Crystal-violet. Martin Freund and Heinrich Beck (*Ber.*, 1904, **37**, 4679—4680).—Crystal-violet, suspended in ether, reacts vigorously with magnesium benzyl chloride to form *hexamethyltriaminotriphenylbenzylmethane*, $CH_2Ph{\cdot}C(C_6H_4{\cdot}NMe_2)_3$, separating from chloroform and alcohol in small, slightly blue crystals melting at 181—182°. Potassium iodide precipitates the crystalline *hydriodide*, melting and decomposing at 267—268°, from its solution in hydrochloric acid. No dye is obtained on oxidation with chloranil or lead peroxide and hydrochloric acid.

C. H. D.

2-Alkyloxypyrimidine Derivatives. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 155732).—The hydrochlorides of the ethers of *iso*carbamide, $R{\cdot}O{\cdot}C(NH_2){:}NH,HCl$, prepared by the action of alcohols and hydrogen chloride on cyanamide (Stieglitz and McKee, Abstr., 1900, i, 340, 431), react with the metallic derivatives of alkyl cyanoacetates to form 2-alkyloxy-derivatives of pyrimidine,

$$\begin{array}{l} \quad\ \ NH{\cdot}CO{\cdot}CH_2 \\ \quad\ \ | \qquad\quad\ | \\ OR{\cdot}C{:}N\text{——}C{:}NH \end{array}.$$

The *2-methoxypyrimidine* derivative, prepared by adding sodium to a solution of ethyl cyanoacetate and *iso*carbamide methyl ether hydrochloride in absolute methyl alcohol, crystallises from hot water or alcohol in colourless needles melting at 228—229° and dissolving readily in alkalis or acids. The 2-ethoxy-derivative is similar, and melts at 247°.

These compounds may be converted into derivatives of hypoxanthine by Traube's method (Abstr., 1900, i, 416). C. H. D.

Preparation of Diethylxanthine. GEORG SCARLAT (*Chem. Centr.*, 1904, ii, 1497; from *Bull. Soc. Sci. Bucarest*, **13**, 155—159).—By the action of phosphorus oxychloride on the solution obtained by heating together a mixture of pyridine and cyanoacetic acid with finely powdered diethylcarbamide, the hydrochloride or phosphate of 6-*imino*-2 : 4-*dioxy*-1 : 3-*diethylpyrimidine*, $CO<\begin{matrix}NEt\text{——}CO\\NEt\cdot C(NH)\end{matrix}>CH_2$, is obtained as a syrup. The base, prepared from the salt by evaporating with ammonia, crystallises from water in needles and melts at 137°. The iso*nitroso*-compound, $C_8H_{12}O_3N_4,H_2O$, crystallises in small, dark red plates and is sparingly soluble in water. 5 : 6-*Diamino*-2 : 4-*dioxy*-1 : 3-*diethylpyrimidine*, obtained by warming the preceding compound with yellow ammonium sulphide, forms yellow crystals, and when boiled with anhydrous formic acid yields 6-*amino*-5-*formylamino*-2 : 4-*dioxy*-1 : 3-*diethylpyrimidine*, $C_9H_{14}O_3N_4$, which crystallises from absolute alcohol in white needles and is readily soluble in water or alcohol; it melts and decomposes at 235°, forming 1 : 3-diethylxanthine, $\begin{matrix}NEt\cdot CO\cdot C\cdot NH\\CO\cdot NEt\cdot C\text{—}N\end{matrix}>CH$, with elimination of water. Diethylxanthine crystallises from water in yellow prisms and melts at 208°.

1 : 3 : 7-Triethylxanthine, $\begin{matrix}NEt\cdot CO\cdot C\cdot NEt\\CO\cdot NEt\cdot C\text{——}N\end{matrix}>CH$, prepared by the action of ethyl iodide and sodium ethoxide (2 mols.) on diethylxanthine, melts at 115° and is readily soluble in alcohol.

E. W. W.

Acetyl Derivatives of Phenylurazole. SALOMON F. ACREE (*Amer. Chem. J.*, 1904, **32**, 606—611. Compare Abstr., 1902, i, 242; 1903, i, 867).—It has been shown (Abstr., 1903, i, 867) that when acetylphenylurazole, prepared by Cuneo's method (Abstr., 1899, i, 9), is treated with diazomethane, 2-acetyl-1-phenyl-4-methylurazole is produced, which melts at 94°, but after heating at 140° melts at 113—115°. The same change takes place when the substance is left for a few months at the ordinary temperature. The product melting at 113—115° is identical with the compound which was obtained by Busch (Abstr., 1901, i, 617) by the action of acetic anhydride and sodium acetate on 1-phenyl-4-methylurazole and was inadvertently stated to melt at 129°.

A few months after the first experiments had been carried out, an attempt was made to prepare a further quantity of the substance melting at 94° from the same sample of acetylphenylurazole, which still showed the same melting point (173°) as before, but only the isomeride melting at 113—115° could be obtained. Numerous experiments have been made with acetylphenylurazole prepared in various ways, but in no case has the labile form of the methyl derivative melting at 94° again been obtained. It is probable that acetylphenylurazole prepared by Cuneo's method consists of a mixture of two substances,

the labile modification, $\left.\begin{matrix}\mathrm{NPh{-}N}\\ \mathrm{CO{\cdot}NH}\end{matrix}\right\rangle\mathrm{C{\cdot}OAc}$, and the stable modification, $\left.\begin{matrix}\mathrm{NPh{\cdot}NAc}\\ \mathrm{CO{-}{-}NH}\end{matrix}\right\rangle\mathrm{CO}$.

The action of acetyl chloride on the silver salt of phenylurazole has been reinvestigated. It is found that acetylphenylurazole is the chief product of the reaction, a small amount of diacetylphenylurazole, which melts at 165°, also being produced. The labile diacetylphenylurazole described by Wheeler and Johnson (Abstr., 1903, i, 693) could not be obtained.

The action of ethyl iodide on silver phenylurazole has also been re-examined (compare Wheeler and Johnson, *loc. cit.*), and it has been found that 3-ethoxy-1-phenylurazole is produced together with a smaller quantity of 3 : 5-diethoxy-1-phenylurazole. E. G.

[Relations between Quinonehydrazones and *p*-Oxyazo-compounds.] WALTHER BORSCHE (*Annalen*, 1904, **336**, 346).—The author had overlooked (Abstr., 1904, i, 1056) Hewitt and Pope's description of *p*-hydroxyazobenzene hydrochloride (Abstr., 1897, i, 517). G. Y.

[Azo-compounds from 3-Hydroxydiphenylamine.] K. OEHLER (D.R.-P. 155044).—The diazonium compounds of naphthionic acid or *β*-naphthylamine-5 : 7-disulphonic acid combine with 3-hydroxydiphenylamine to form azo-compounds, which yield very fast brown dyes on treatment with chromium salts, the hydroxy-group probably occupying the ortho-position with respect to the azo-group. C. H. D.

Azo-compounds from Sulphonic Acids of *a*-Amino-*β*-naphthol. CHEMISCHE FABRIKEN VORM. WEILER-TER-MEER (D.R.-P. 155083).—Azo-compounds of acid character, yielding dark lakes with sodium dichromate or ferric acetate, are obtained on diazotising the mono- or di-sulphonic acids of *a*-amino-*β*-naphthol in the presence of organic acids only, and combining the diazo-compounds with resorcinol in alkali hydroxide solution. C. H. D.

The Copper Compound of *p*-Nitroaniline-Red. WLADIMIR SCHAPOSCHNIKOFF and V. SVIENTOSLAVSKI (*Zeit. Farb. Text. Ind.*, 1904, **3**, 422—426).—The same deep brown dye is obtained by boiling *p*-nitroaniline-red with aqueous copper sulphate containing ammonia as is formed on adding a mixture of alkaline sodium *β*-naphthoxide, tartaric acid, and aqueous cupric chloride to diazotised *p*-nitroaniline; after suitable purification, the compound has the composition of the *copper* salt, $(NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}O)_2Cu$, of *p*-nitrobenzeneazo-*β*-naphthol. In a similar way, the *copper* salt of benzeneazo-*β*-naphthol may be prepared. That these substances are merely the copper salts, as supposed, is shown by the fact that on decomposition with hydrochloric acid they regenerate the hydroxyazo-compounds. W. A. D.

Azodiphenylmethane : a Correction. PAUL FREUNDLER (*Bull. Soc. chim.*, 1905, [iii], **33**, 80—81. Compare Abstr., 1903, i, 585).—It is shown that the substance obtained by the author by heating benzene-*o*-azobenzyl alcohol at 130° is not, as was supposed, azodiphenylmethane, but a molecular combination of azobenzene and phenylindazole. The presence of azobenzene is probably due to the formation of a hydroxylamine derivative along with benzene-*o*-azobenzyl alcohol in the condensation of nitrosobenzene with *o*-aminobenzyl alcohol and the subsequent dehydration of this. T. A. H.

***p*-Nitrobenzeneazo-*o*-tolueneneazo-β-naphthol.** FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 155396).—*p*-Nitrobenzeneazo-*o*-toluidine may be diazotised at 15—20°, and then yields a garnet-red azo-compound with β-naphthol. If the fabric is first treated with β-naphthol and afterwards with the diazo-solution, the dye is deposited in the fibre, and then resembles "alizarin garnet." The colour is completely removed by means of formaldehyde-sodium hydrogen sulphite. C. H. D.

Disazo-dyes from 6-Amino-α-naphthol-3-sulphonic Acid. K. OEHLER (D.R.-P. 155740).—In the preparation of disazo-compounds from 6-amino-α-naphthol-3-sulphonic acid (Abstr., 1904, i, 809), nitro-*o*-aminophenol may be replaced by chloro-*o*-aminophenol. The combination occurs more slowly than when nitro-compounds are employed, but the properties of the dyes produced are similar.

C. H. D.

Formation of Hydrogen Cyanide by the Oxidation of Proteids. R. H. ADERS PLIMMER (*J. Physiol.*, 1904, **32**, 51—58. Compare Abstr., 1904, i, 538).—By the oxidation of albumins with chromic acid, a constant amount of hydrogen cyanide is evolved, which varies for each albumin; the amount thus obtained is usually greater than in oxidation by Neumann's nitric acid mixture. The products of proteolysis give a rather greater amount than the albumins themselves. The hydrogen cyanide arises from the glycine and aspartic acid, but the other amino-acids also give rise to a small quantity which, however, is negligible in comparison. W. D. H.

Amyloid. CARL NEUBERG (*Chem. Centr.*, 1904, ii, 1576—1577; from *Verh. Deut. Path. Ges.*, 1904, 19—32).—According to Krawkow, amyloid is a compound of chondroitinsulphuric acid with a proteid. The latter differs materially from the albumin of the cell, and more nearly resembles the protamines or histones. The results of the hydrolysis of a liver amyloid showed that it yielded 0·8 per cent. of glycollic acid, 22·2 of leucine, 3·8 of glutamic acid, 4·0 of tyrosine, 3·1 of pyrollidine-2-carboxylic acid, 13·9 of arginine, and 11·6 of lysine; histidine was not present. The leucine consisted of a mixture of amino*iso*butylacetic acid and F. Ehrlich's *iso*leucine. Complete precipitation of pyrollidine-2-carboxylic acid from a solution in methyl alcohol may be effected by means of a solution of mercury acetate in methyl alcohol to which potassium methoxide has

been added. Since it is improbable that *d*-tyrosine is a component of amyloid or that racemisation takes place in the process of decomposition, it must be assumed that the fundamental constituent is a substance which is comparatively stable towards acids and resembles the protamines or Siegfried's kyrines. The monoamino-acids, which are only feebly combined with this substance, are liberated at once, and a portion of them is rendered inactive by the action of boiling sulphuric acid. The resemblance to the histones is supported by the fact that amyloid is always found in combination with an acid. Amyloid can no longer be regarded as a particular coagulation form of albumin. It has been shown that it is attacked by pepsin and trypsin in the ordinary way, although the action is somewhat slower than in the case of normal albuminous substances. Amyloid livers are thus subject to autolysis in the typical way, and the possibility of resorption cannot be doubted. Whilst the percentage composition of amyloids from different sources varies but little, the forms in which the nitrogen and sulphur are contained are by no means the same in each case; the latter may be present not only in the sulphate form, but also in a state of combination similar to that in which it is found in cystine. In the following table, the samples (1), (2), and (3) refer respectively to amyloids from liver, spleen, and a normal human aorta:

	C.	H.	N.	S.	Percentage of total N present as			Total S consists of	
					N in mon-amino-acids.	N in di-amino-acids.	N in amide form.	S in sulphate.	Non-oxidised S.
1	50·1	7·0	14·1	2·6	43·2	51·2	4·9	1·7	0·9
2	49·3	7·1	14·1	1·8	30·6	57·0	11·2	1·8	0·0
3	49·6	7·2	14·4	2·3	54·9	36·0	8·8	0·4	1·9

Proteids of a pronounced basic character always occur in places where normal tissue is undergoing change, and amyloid is a product of the metamorphosis of albuminous substances. Amyloids from the liver, spleen, and aorta may possibly represent different phases of the process of change which culminates in the formation of the typical liver amyloid. E. W. W.

Preparation of Bromolecithin. Aktien-Gesellschaft für Anilin-Fabrikation (D.R.-P. 156110).—Lecithin readily combines with bromine in chloroform solution, the amount of bromine taken up varying with the source of the lecithin employed. Lecithin obtained from egg-yolk absorbs 30 per cent. of its weight of bromine. On evaporation under reduced pressure, the product is obtained as a colourless, waxy mass. Unlike lecithin, bromolecithin is not hydrolysed by the intestinal juice. C. H. D.

Iodo-derivatives of Lecithin. J. D. Riedel (D.R.-P. 155629).—Iodo-derivatives of lecithin are obtained by the action of iodine chloride, or of mixtures producing iodine chloride, on lecithin. The products dissolve readily in ether or warm alcohol, and swell in water; they may contain as much as 50 per cent. of iodine. Alkalis decompose them, yielding choline, glycerolphosphoric acid, and fatty iodo-acids. The iodine is contained in the fatty acid residue. Choline yields only an unstable additive compound with iodine chloride. Products containing 5—20 per cent. of iodine find therapeutic application. C. H. D.

Hæmocyanin. II. Martin Henze (*Zeit. physiol. Chem.*, 1904, **43**, 290—298. Compare Abstr., 1901, i, 783).—The distribution of the nitrogen in the hæmocyanin molecule has been determined by Hausmann's method with the following results: total = 16·09; as ammonia, 0·93; as humin, 0·43; diamide nitrogen, 4·45; and monamide nitrogen, 10·20 per cent. When hydrolysed with 33 per cent. sulphuric acid, the following products are obtained: histidine, lysine, glutamic acid, tyrosine, and leucine. Arginine could not be isolated, and a reducing sugar could not be detected among the products of hydrolysis. J. J. S.

Velocity of Enzymatic Reactions. II. Reginald O. Herzog (*Zeit. physiol. Chem.*, 1904, **43**, 222—227. Compare Abstr., 1904, ii, 164, 506).—Largely a reply to Henry (*Compt. rend. Soc. Biol.*, 1904, **57**, 173). Further experiments are described, which tend to show that in solutions of equal viscosity the rate of inversion of sucrose by invertase is practically the same. J. J. S.

Diastasic Coagulation of Starch. Auguste Fernbach and Jules Wolff (*Compt. rend.*, 1904, **138**, 1217—1219. Compare Abstr., 1904, i, 211, 228, 294, 374).—The diastasic coagulation of starch is only possible when the starch is in a state of liquefaction, produced either by a liquefying diastase such as amylase, or artificially, by heating under pressure. A 4·5 per cent. solution of starch is coagulated by an extract of malt which has not been heated, or by a mixture of extracts of barley, wheat, or rye which have not been heated with a malt extract which has been heated at 75°, a temperature at which the amylo-coagulase is destroyed, whilst the liquefying property of the amylase is preserved. Further, starch paste which has been liquefied by heating under pressure at 145° is coagulated by barley extract. M. A. W.

Phenyl Derivatives of Elements of the Phosphorus Group. Paul Pfeiffer [with Ida Heller and H. Pietsch] (*Ber.*, 1904, **37**, 4620—4623. Compare Pfeiffer and Schnurmann, Abstr., 1904, i, 232; Pfeiffer and Truskier, *ibid.*, i, 544).—Triphenylphosphine is conveniently prepared by the action of magnesium phenyl bromide on phosphorus trichloride in ethereal solution; it crystallises from a mixture of alcohol and ether in colourless prisms or plates, and melts at 78·5°. Triphenylarsine, triphenylstibine, tri-*p*-tolylstibine, and triphenylbismuthine were all prepared, with a good yield, by a similar method. W. A. D.

Organic Chemistry.

Action of Acetylene on Solutions of Mercuric Chloride. HEINRICH BILTZ (*Ber.*, 1905, **38**, 133—136. Compare this vol., i, 2; Hofmann, Abstr., 1898, i, 635; 1899, i, 97, 485; this vol., i, 2).—A criticism of Hofmann's work and a claim for priority. G. Y.

Tetraiodoethylene and Di-iodoethylene. ERNST ERDMANN and HUGO ERDMANN (*Ber*, 1905, **38**, 237—240).—Tetraiodoethylene is conveniently prepared in quantity by a modification of Maquenne's method (Abstr., 1893, i, 449). Water is slowly allowed to drop into a well-stirred mixture of iodine, calcium carbide and benzene, the temperature being kept below 45°. The product is freed from di-iodoethylene by distillation with steam and recrystallised from benzene. The authors agree with Biltz (Abstr., 1897, i, 389) that the di-iodoethylene is formed as a by-product. Unfavourable results were obtained on using tetraiodoethylene in place of iodoform in the treatment of wounds. E. F. A.

Action of Chlorine on *iso*Butylene. S. A. POGORŽELSKY (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 1129—1184).—The author's experiments, described in detail in this paper, show that the reaction between chlorine and *iso*butylene may, so far as the products first formed are concerned, be represented as follows: $m CMe_2{:}CH_2 + n Cl_2 =$ $CMe_3Cl + CH_2Cl{\cdot}CMe{:}CH_2 + CMe_2Cl{\cdot}CH_2Cl + CH_2Cl{\cdot}CMe{:}CHCl + CH_2Cl{\cdot}CMeCl{\cdot}CH_2Cl + \ldots$ The first of these products, CMe_3Cl, requires for its formation the presence of hydrogen chloride, but it appears as a product of the total interaction of chlorine and *iso*butylene.

The water in presence of which the chlorination of the *iso*butylene took place was found to contain small quantities of trimethylcarbinol, *iso*butenol, and *iso*butyleneglycol. T. H. P.

Addition of Iodine Chloride to *iso*Butylene. A. W. ISTOMIN (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 1199—1208).—The addition of iodine monochloride to *iso*butylene, in the cold, avoiding an excess of the latter, yields a small quantity of *iso*butylene chloride, but mainly iso*butylene chloroiodide* [*β-chloro-α-iodo-β-methylpropane*], $CMe_2Cl{\cdot}CH_2I$, which boils at 62—63° under 20—22 mm. pressure and has the sp. gr. 1·7502 at 15°/4°. On heating with methyl alcohol, it yields the *ether*, $OMe{\cdot}CMe_2{\cdot}CH_2I$, which boils at 69—70° under 20—22 mm. pressure or, with decomposition, at 165—166° under 760 mm. pressure. This ether reacts with magnesium in presence of a small quantity of magnesium methiodide, yielding *βε-dimethylhexylene-βε-glycol dimethyl ether*, $OMe{\cdot}CMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}CMe_2{\cdot}OMe$, which boils at 190—192° under 780 mm. pressure and has the normal molecular weight in

freezing benzene; when treated with hydrobromic acid, this compound yields di*iso*crotylic bromide (Pogorželsky, Abstr., 1899, i, 785).

T. H. P.

Action of Water on Hexylene Dibromide (from Mannitol). HEINRICH KLARFELD (*Monatsh.*, 1905, **26**, 83—88. Compare Hecht, *Annalen*, 1881, **209**, 311).—When heated with water in a sealed tube at 160—170° for nine hours, hexylene dibromide (b. p. 91° under 17 mm. pressure) yields hexylene and a mixture of methyl butyl ketone and ethyl propyl ketone.

G. Y.

Tridecyl Alcohol. J. BLAU (*Monatsh.*, 1905, **26**, 89—109).—Myristamide (Reimer, Abstr., 1885, 1197) prepared by Aschan's method (Abstr., 1889, i, 14) melted at 105—107°, or after recrystallisation at 102°. Some preparations made with commercial phosphorus trichloride melted at 85°. The action of bromine in carbon tetrachloride solution on myristamide dissolved in methyl alcohol followed by sodium methoxide leads to the formation of *methyl tridecylcarbamate*,

$$C_{13}H_{27}\cdot NH\cdot CO_2Me,$$

which crystallises in small, white leaflets and melts at 53—54°, and myristyltridecylcarbamide, $C_{13}H_{27}\cdot NH\cdot CO\cdot NH\cdot CO\cdot C_{13}H_{27}$, which crystallises in large, silky leaflets and melts at 103°. Tridecylamine, $C_{13}H_{27}\cdot NH_2$, formed by distilling the urethane or the carbamide with potassium hydroxide, absorbs moisture and carbon dioxide from the atmosphere and solidifies to a white mass; the hydrochloride, $C_{13}H_{29}N,HCl$, crystallises in small needles and decomposes at 160°; the platinichloride, $(C_{13}H_{29}N)_2,H_2PtCl_6$, crystallises in yellow spangles and decomposes at 205°, [compare Reimer and Will, Abstr., 1885, 1197; Lutz, Abstr., 1886, 685]. *Tridecyl alcohol*, $C_{13}H_{27}\cdot OH$, prepared by the action of silver nitrite and hydrochloric acid on the amine in aqueous solution, melts at 30·5°, boils at 155—156° under 15 mm. pressure, and has a sp. gr. 0·8223 at 31°/4°. On oxidation with potassium dichromate and sulphuric acid, the alcohol yields tridecoic acid, which melts at 40°.

G. Y.

Reduction of Dimethyltrimethylene Glycol ($\beta\beta$-Dimethylpropan-$\alpha\gamma$-diol) by means of Fuming Hydriodic Acid. PAUL MEYERSBERG (*Monatsh.*, 1905, **26**, 41—51. Compare Apel and Tollens, Abstr., 1896 i, 115; Just, Abstr., 1896, i, 403).—When heated with an excess of fuming hydriodic acid in a sealed tube at 100—110° for about 30 hours, $\beta\beta$-dimethyltrimethylene glycol yields the iodohydrin and *tert.*-butylcarbinyl iodide (Tissier, Abstr., 1893, i, 542). The iodide distils unchanged at 42—44° under 20 mm., at 52° under 35 mm. pressure, has a sp. gr. 1·5317 at 13°, or 1·463 at 26°, and, on treatment with silver acetate in glacial acetic acid solution and hydrolysis of the product with dilute aqueous potassium hydroxide, yields *tert.*-butylcarbinol. When boiled with aqueous potassium carbonate, in a reflux apparatus, the iodide yields only a small proportion of the carbinol, the remainder being converted probably into the volatile amylene.

G. Y.

Preparation of Xanthogen Compounds. L. A. TSCHUGAEFF (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 1253—1258).—The preparation of xanthogen compounds by the formation of the sodium alkyloxide

and subsequent action of carbon disulphide and an alkyl iodide requires a long-continued heating of the alcohol with sodium at a high temperature, and is often accompanied by isomeric change and the formation of resinous products. The author finds that by using potassium in place of sodium the time required for the reaction is considerably shortened. The fact that primary and secondary alcohols liberate *tert.*-amyl alcohol (dimethylethylcarbinol) from potassium *tert.*-amyloxide may also be used to simplify the method of preparation of xanthogen compounds, as the potassium compounds of alcohols of the terpene series may be prepared in this way. T. H. P.

Action of Dilute Acids on Pinacones. Adolf Lieben (*Monatsh.*, 1905, **26**, 35—39).—Contrary to what might be expected from Erlenmeyer's theory (*Ber.*, 1881, **14**, 322), the results obtained by Zumpfe (Abstr., 1904, i, 291) and Kohn (following abstract) suggest that the pinacolin formation takes place with those pinacones only which contain the grouping ⁚CMe·OH. G. Y.

Action of Dilute Sulphuric Acid on Propionepinacone. Siegfried Kohn (*Monatsh.*, 1905, **26**, 111—118. Compare Zumpfe, Abstr., 1904, i, 291; Lieben, preceding abstract).—When boiled with dilute sulphuric acid for five hours in a reflux apparatus, propionepinacone yields two products.

(1) A *hydrocarbon*, $C_{10}H_{18}$, which is a colourless liquid with a pleasant odour, boils at 153—154°, is insoluble in water, but easily soluble in alcohol, ether, or chloroform, and forms an *additive* compound with 1 mol. of bromine.

(2) An oxide, $C_{10}H_{20}O$, which is a yellow, mobile liquid with a characteristic odour; it boils at 189—190°, does not form an oxime, does not react with zinc ethyl at 100° or with water at 210—220°, and, when oxidised with potassium permanganate in alkaline solution, yields α-ethylbutyric acid and an *acid*, $C_9H_{16}O_3$, which forms a *silver* salt, crystallising in long, white needles, and therefore is probably an αδ-oxide. G. Y.

Action of Organic Acids on Metals of the Cerium and Yttrium Groups. Theodor H. Behrens (*Rec. trav. chim.*, 1904, **23**, 413—418. Compare Abstr., 1902, ii, 80).—The formates of metals of the yttrium group crystallise in pentagonal dodecahedra. When aqueous solutions of the salts are evaporated at the boiling point until of syrupy consistence, they become turbid after some hours, and then, on addition of water, deposit crystals which are from 5 to 8μ long, dissolve with difficulty in water and readily in formic acid, and leave a yellow oxide on ignition. These reactions are similar to those of Marignac's terbium, the existence of which the author doubts. Erbium can be detected by examining the absorption spectrum and iron by the usual colour reactions.

When acetic acid is added to aqueous solutions of formates of the yttrium group, double salts are precipitated in the form of transparent rhombs, 30 to 50μ long, with an acute angle of 63°, optically negative

in the direction of the long diagonal, and showing well-marked colours with polarised light.

The metals of the yttrium group give salts with the aliphatic hydroxy-acids crystallising in radiating spheroids, 50 to 80μ long, brown by transmitted light, and showing a cross when placed between the nicols. Needles 120μ long can be obtained from dilute solutions. Metals of the cerium group as well as thorium and zirconium give readily soluble salts with these acids.

Ammonium fumarate gives precipitates of rhomboidal tablets with both the cerium and yttrium groups, the crystals in the former group being from 50 to 70μ, and in the latter from 120 to 150μ long. In both cases, the acute angles of the rhombs are 64—66°, and the angle of extinction 19°, but the fumarates of the yttrium group are the more soluble. Mesaconic acid gives with cerium or lanthanum nitrate spheroidal aggregates of rod-like crystals 15μ long, and with yttrium or erbium nitrate rectangular rods 20 to 30μ long, with angle of extinction 36° and often grouped into bunches. The mesaconates of the last two metals are more soluble than those of the former two.

T. A. H.

Preparation of Anhydrides of Chloroacetic Acids. THOMAS S. PATTERSON (*Ber.*, 1905, **38**, 210—213. Compare Buckney and Thomsen, *Ber.*, 1877, **10**, 698; Antoine, *J. Pharm. Chim.*, 1883, [v], **8**, 417; Bischoff and Walden, Abstr., 1895, i, 17).—Perfectly anhydrous sodium carbonate has no action on freshly-prepared chloroacetyl chloride, but when the carbonate has been exposed to the air for a short time it reacts vigorously with the chloride yielding varying amounts of anhydride.

The following boiling points for the anhydride are given:

Pressure	24	36	51	62	104	116 mm.
Boiling point	126°	135°	144°	149°	161°	163°

For chloroacetic acid:

Pressure	18	36	68	101	152	207 mm.
Boiling point	93°	108°	121°	130·1°	140·5°	149°

For dichloroacetic acid:

Pressure	21	24	36	71	88	142	164 mm.
Boiling point	99°	102·5°	111·5°	125°	129°	140°	144°

J. J. S.

Migration of the Ethylenic Linking in Unsaturated Open-chain Acids. EDMOND E. BLAISE and A. LUTTRINGER (*Compt. rend.*, 1905, **140**, 148—150).—Fittig has shown (Abstr., 1895, i, 204) that the $\alpha\beta$-unsaturated acids are converted by the action of alkalis into the corresponding $\beta\gamma$-isomerides; in the present paper, the authors show that the action of concentrated or 80 per cent. sulphuric acid at 0° on the α-ethyl-, α-propyl-, α-*iso*propyl-, α-butyl-, α-heptyl-acrylic acids, on α-methyl-β-ethylacrylic acid, or on $\alpha\beta$-hexenoic acid causes the ethylenic linking to migrate from the shorter into the longer carbon chain, giving an $\alpha\beta$- or a $\beta\gamma$-unsaturated isomeride, the latter forming

a γ-lactone (equation I). The mechanism of the reaction appears to involve successive hydrations and dehydrations, and in certain cases the ketone resulting from the decomposition of the intermediate α-hydroxy-acid has been isolated (equation II):

$$\text{I. } CH_2R{\cdot}CH_2{\cdot}C(CO_2H){:}CH_2 \longrightarrow CH_2R{\cdot}CH_2{\cdot}CMe(OH){\cdot}CO_2H \longrightarrow CH_2R{\cdot}CH{:}CMe{\cdot}CO_2H \longrightarrow CH_2R{\cdot}CH(OH){\cdot}CHMe{\cdot}CO_2H \longrightarrow CHR{:}CH{\cdot}CHMe{\cdot}CO_2H \longrightarrow CHR(OH){\cdot}CH_2{\cdot}CHMe{\cdot}CO_2H \longrightarrow \begin{matrix} CHMe{\cdot}CO \\ | \\ CH_2\text{-}CHR \end{matrix}\!\!>\!O.$$

$$\text{II. } CH_2R{\cdot}CH_2{\cdot}C(CO_2H){:}CH_2 \longrightarrow CH_2R{\cdot}CH_2{\cdot}CMe(OH){\cdot}CO_2H \longrightarrow CH_2R{\cdot}CH_2{\cdot}CO{\cdot}CH_3.$$

When the carbon atom in the γ-position to the carboxyl groups is primary, the $\alpha\beta$-unsaturated acid is formed, thus α-ethylacrylic acid yields tiglic acid and methyl ethyl ketone; when the carbon atom in the β-position is tertiary, the corresponding ketone is the only product and α-*iso*propylacrylic acid gives methyl *iso*propyl ketone, and when the carbon atom in the γ-position is secondary, a ketone and a γ-lactone are produced. M. A. W.

Condensation Products from Fatty Aldehydes and Negatively-substituted Acetic Acids. EMIL KNOEVENAGEL (D.R.-P. 156560).—Fatty aldehydes combine with negatively substituted acetic acids, such as malonic, cyanoacetic, acetoacetic, benzoylacetic, and acetonedicarboxylic acids in the presence of small quantities of ammonia or primary or secondary amines.

Valeraldehyde and malonic acid, with a little piperidine, yield *δ-methylhexenoic acid*, consisting of a mixture of the Δ^{α}- and Δ^{β}-acids, boiling at 127—132° under 25 mm. pressure. When 2 mols. of malonic acid are employed, the product is *β-*iso*butylglutaric acid*, which melts at 48° and boils at 205—210° under 15 mm. pressure. Valeraldehyde and cyanoacetic acid yield *α-cyano-δ-methyl-*Δ^{α}*-hexenoic acid*, melting at 53°, and *αα-dicyano-β-*iso*butylglutaric acid*, melting at 162°. Heptaldehyde and malonic acid yield nonylenoic acid; heptaldehyde and cyanoacetic acid yield *αγ-dicyano-β-hexylglutaric acid*, which melts at 142°. Citral also condenses with malonic or cyanoacetic acid to form citrylidene derivatives.

The condensation of aromatic aldehydes with these acids (Abstr., 1899, i, 144) requires the addition of a larger quantity of the base. C. H. D.

Changes effected by Time on Hydrocarbon Substances of Organic Origin. MARCELLIN BERTHELOT (*Compt. rend.*, 1905, **140**, 177—183).—From the viscous fatty matter extracted from an Egyptian vase belonging probably to the XVIIIth Dynasty (B.C. 1600 to 1370), the author has isolated the acids $C_5H_{10}O_3$ and $C_4H_8O_3$ of the hydroxystearic series in the form of their soluble crystalline calcium salts, the insoluble residue consisting of a mixture of acids of the hydroxyoleic series, $C_nH_{2n-2}O_3$, and of bitumens or resins, $(C_5H_{10}O)_n$; these acids are possible products of the gradual oxidation of oil of ricinus, and it is probable that this oil, together

with balms, resins, bitumens, &c., constituted the original contents of the vases. M. A. W.

Sodium Acetoacetate and the Formation of Analogous Salts in Solution. JULIUS W. BRÜHL and HEINRICH SCHROEDER (*Ber.*, 1905, **38**, 220—226. Compare Abstr., 1904, i, 646, 969).—Ethyl acetoacetate was mixed with the equivalent quantity of sodium ethoxide in absolute alcohol, and the spectrochemical functions of the components of the mixture determined before and after mixing. A very great change in the dispersion takes place on mixing. Taken in conjunction with the results obtained with the esters of camphorcarboxylic acid (*loc. cit.*), it is beyond doubt that ethyl acetoacetate during salt formation is completely enolised, change taking place from a non-conjugated linking to a conjugated system :

$$O\colon CMe\cdot CH_2\cdot CO_2Et \longrightarrow ONa\cdot CMe\colon CH\cdot CO_2Et.$$

This is discussed at some length in connection with the theory of Willstätter and Pummerer (Abstr., 1904, i, 1043) that the salts of ethyl acetoacetate with sodium ethoxide are additive compounds of the type $CO_2R\cdot CH_2\cdot CR(OEt)\cdot ONa$.

It is shown, however, that the whole optical behaviour of sodium acetoacetate can only be explained on the theory that isomeric change takes place. In general, the esters of β-ketonic acids are instantly enolised when they form salts. E. F. A.

Ethyl Citrylideneacetoacetate. EMIL KNOEVENAGEL (D.R.-P. 156115).—Ethyl citrylideneacetoacetate (Abstr., 1902, i, 342) does not yield a perfume on inversion with acids. If heated for several hours at 160° with or without the addition of water, however, the ester undergoes a change, the boiling point and specific gravity being raised. On inverting the product by means of acids, a compound is obtained, boiling at 150—190° under 12 mm. pressure, which may be employed as a perfume. C. H. D.

Intramolecular Migration of Acyl Groups. WILHELM WISLICENUS (*Ber.*, 1905, **38**, 546—548. Compare Abstr., 1901, i, 187; 1902, i, 72; Bouveault and Bongert, Abstr., 1903, i, 145; Dieckmann and Stein, Abstr., 1904, i, 873).—The author has heated ethyl *O*-acetylacetoacetate, in total absence of any alkali, in a platinum tube at 240° for three hours, and confirms the previous statement that under these conditions about 1 per cent. of the *O*-acetyl ester is converted into the *C*-derivative. G. Y.

Action of Bases on Chloral Hydrate. JOHANNES E. ENKLAAR (*Rec. trav. chim.*, 1904, **23**, 419—439).—Reicher has shown that the rate of decomposition of chloral hydrate by bases is proportional to the excess of base used over that necessary to form with the chloral hydrate a salt of the type $CCl_3\cdot CH(OK)\cdot OH$ (*Maandblaad*, 1885, 18). The author confirms this observation, and suggests that the mechanism of the reaction is either that this salt breaks down into chloroform and a formate, or that the complex negative ion, $CCl_3\cdot CH(OH)\cdot O\cdot$, produced by its dissociation, gives rise to chloroform

and the negative ion of formic acid, the reaction in either case being unimolecular and brought about by catalysis under the influence of the -OH ions of the excess of the base used. The former explanation is considered the more probable since the reaction velocity is greater in presence of neutral salts of the base used. It is assumed that the addition of such salts diminishes the dissociation of the chloral hydrate salt and increases the total number of positive ions of the base, and that these positive ions act as accelerators of the catalysing action of the -OH ions. T. A. H.

Condensation of *n*-Butaldehyde by means of Dilute Sulphuric Acid. Adolf Gorhan (*Monatsh.*, 1905, **26**, 73—82. Compare Bauer, Abstr., 1904, i, 279; Kadiera, Abstr., 1904, i, 466). —When heated with 10—40 per cent. sulphuric acid at 100—200° for 8—30 hours, or when heated with fuming hydrochloric acid at 90° for four hours, or when heated in a reflux apparatus at 85—90° for eight hours, *n*-butaldehyde is partially converted into Raupenstrauch's α-ethyl-β-propylacraldehyde (Abstr., 1887, 794) and an unsaturated *aldehyde*, $C_{12}H_{22}O_2$, which is a viscid oil and boils at 160—162° under 12 mm. pressure. It has a pleasant odour, reduces ammoniacal silver solutions, forms a crystalline precipitate with phenylhydrazine, and with bromine in chloroform solution at low temperatures yields the *additive* compound $C_{12}H_{22}O_2Br_2$. G. Y.

Condensation of Form*iso*butaldol with Acetaldehyde. Alois Schachner (*Monatsh.*, 1905, **26**, 65—72. Compare Wessely, Abstr., 1900, i, 428).—The action of form*iso*butaldol on acetaldehyde in presence of aqueous potassium carbonate leads to the formation of the *product* $OH\cdot CH_2\cdot CMe_2\cdot CH(OH)\cdot CH_2\cdot COH$, which in the solid state has the bimolecular formula $(C_7H_{14}O_3)_2$ (compare Kohn, Abstr., 1900, i, 274). It crystallises in sheaves of white needles, melts at 84°, is more soluble than form*iso*butaldol in water or the ordinary organic solvents, does not form an additive compound with bromine, and on distillation decomposes into form*iso*butaldol and acetaldehyde. G. Y.

Chloromalonaldehyde. Walter Dieckmann and Ludwig Platz (*Ber.*, 1905, **38**, 339. Compare this vol., i, 117).—An acknowledgment of priority. W. A. D.

An Isomeride of Trichloroacetone. Gustave Perrier and Eugène Prost (*Compt. rend.*, 1905, **140**, 146—148).—An attempt to replace the chlorine in chloral by the grouping OEt by the action of aluminium ethoxychloride, $Al_2Cl_3(OEt)_3$ (compare Perrier, Abstr., 1901, i, 442), was unsuccessful, the product obtained being an isomeride of trichloroacetone, $C_3H_3OCl_3$, boiling at 182—187° under 764 mm. or at 101—103° under 30 mm. pressure, having a sp. gr. 1·423 at 15° and an odour similar to that of the terpenes. It yields chloral when warmed with sulphuric acid, chloroform when oxidised by chromic mixture, or carbylamine when heated with a mixture of potassium hydroxide, aniline, and alcohol. All these reactions show

that the three atoms of chlorine in the compound are associated with the same carbon atom, and as it differs from trichloroacetone in respect of its insolubility in water and in not being attacked by hot or cold ammonia, the authors suggest the following provisional constitutional formula for the compound $CCl_3\cdot CH<\overset{CH_2}{\underset{O}{|}}$. M. A. W.

Chlorination of Methyl Ethyl Ketone. ANDRÉ KLING (*Compt. rend.*, 1905, **140**, 312—314. Compare Vladesco, 1892, 424, 810; Reymenant, 1901, i, 126).—The action of chlorine on methyl ethyl ketone in presence of water and calcium carbonate leads to the formation of two monochloro-substitution products. The action takes place most regularly at 60—70°. At low temperatures, the action frequently only begins when a considerable quantity of chlorine has been absorbed by the solution, and there is then danger of explosion. The products of incomplete chlorination are the same when the ketone is acted on by sulphuryl chloride, by free chlorine, or by chlorine in presence of iodine, but the best results are obtained by the first method.

The two products can be separated by repeated fractionation. The one which boils at 40—41° under 30 mm. and at 114—117° under 760 mm. pressure is *methyl α-chloroethyl ketone*, $CH_3\cdot CHCl\cdot COMe$. The other boils at 59—60° under 30 mm. and at 134—136° under 760 mm. pressure, and is *chloromethyl ethyl ketone*, $COEt\cdot CH_2Cl$, for on converting it into the corresponding alcohol and reducing this, the glycol,

$$OH\cdot CHEt\cdot CH_2\cdot OH,$$

is obtained. The substance obtained by Reymenant, and stated to boil at 125°, was probably a mixture of these two substances. H. M. D.

New Method of Synthesising Saturated Ketones by Catalytic Reduction. GEORGES DARZENS (*Compt. rend.*, 1905, **140**, 152—153).—Aliphatic unsaturated ketones of the type $C_nH_{2n-2}O$ are converted into the saturated ketones, $C_nH_{2n}O$, by direct hydrogenation at 180—190° in the presence of nickel obtained by reducing nickel oxide at 245—250° (compare this vol., i, 66), and the following ketones were thus prepared: methyl *iso*butyl ketone from mesityl oxide; methyl *iso*amyl ketone from methylhexenone, and methyl *iso*hexyl ketone from natural methylheptenone, or from the synthetical compound. M. A. W.

Addition of Hypochlorous Acid to Allene Hydrocarbons. II. F. W. SMIRNOFF (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 1184—1199. Compare Abstr., 1904, i, 214).—The action of hydrochlorous acid on unsymmetrical dimethylallene yields, as principal product, *chloromethyl hydroxy*iso*propylketone*, $OH\cdot CMe_2\cdot CO\cdot CH_2Cl$, which boils at 84—85° under 10 mm. pressure; the *acetyl* derivative, $OAc\cdot CMe_2\cdot CO\cdot CH_2Cl$, forms crystals melting at 47·5° and boiling at 102—104° under 10 mm. pressure, and the *phenylosazone*,

$$OH\cdot CMe_2\cdot C(N_2HPh)\cdot CH{:}N_2HPh,$$

separates from alcohol in golden-yellow crystals melting at 141°.

The other products of the reaction are: (1) chloromethyl chloro*iso*-

propyl ketone and (2) $\beta\beta$-dichloro-$\alpha\delta$-dihydroxy-γ-methylbutane,

$$OH\cdot CMe_2\cdot CCl_2\cdot CH_2\cdot OH,$$

which forms crystals melting at 151°, dissolves readily in alcohol or ether, and to a less extent in benzene or water, and reduces Fehling's solution in the cold.

The above products are what would be expected, according to theory, to be formed in this reaction. T. H. P.

Birotation of Galactose. Gunnar Heikel (*Annalen*, 1905, 338, 71—104).—The most probable cause of the birotation of an aldhexose is the existence of two stereoisomeric lactone forms, which are very readily transformable into one another, possibly through the intermediary stage of the aldose. This supposition has found support in the fact that pyridine solutions of dextrose of different rotatory powers yield two penta-acetates (Abstr., 1904, i, 657).

On investigating galactose, it was found that an aqueous solution had $[\alpha]_D$ 80·8° at 20°, but in anhydrous pyridine at first $[\alpha]_D$ 170°, and finally $[\alpha]_D$ 55·6° Solid galactose, when acetylated in pyridine solution at 0°, yielded a *penta-acetate*, $C_6H_7O_6Ac_5$, which could not be crystallised and had $[\alpha]_D$ + 71·8° in benzene at 20°. The already known β-penta-acetate, prepared by acetylating at the ordinary temperature, melts at 141·5—142°, and has $[\alpha]_D$ 59·2°, whilst an amorphous substance formed at the same time has $[\alpha]_D$ 60·8°. When the acetylation is carried out at 100°, the same β-acetate and a product having $[\alpha]_D$ 28·6°, and when the acetylation is carried out in pyridine at 50—60°, the β-acetate and a product having $[\alpha]_D$ 49·7°, are obtained. The acetate having $[\alpha]_D$ 71·8° is probably the pure isomeric α-acetate, whereas the other amorphous forms are taken to indicate the existence of a third, γ-acetate. The behaviour of galactose dissolved in boiling pyridine confirms this supposition, since an initial rotation of $[\alpha]_D$ 31° changes slowly into the rotation of $[\alpha]_D$ 59·26° when the solution has cooled.

It seems probable that the γ-penta-acetate corresponds with the aldehyde form of the sugar. In aqueous solution, the α-galactose with the high rotatory power changes into a mixture of the β- and γ-galactoses. At a higher temperature, the equilibrium changes in favour of the γ-galactose. Attempts to convert the penta-acetates into different methylglucosides yielded only the mixture of known glucosides. K. J. P. O.

[Birotation of Dextrose.] Robert Behrend (*Annalen*, 1905, 338, 105—107. Compare preceding abstract).—Since Heikel has shown that at least three modifications of galactose exist, it is probable that dextrose also possesses an aldehyde form. In order to demonstrate that the birotation of dextrose is not due to hydration, dextrose was dissolved in anhydrous pyridine at 0° and the rotatory power determined after given intervals of time. The change was found to be a reaction of the first order; if it was a case of hydration, the reaction would have been one of the second order; further, it is not probable that dextrose would take up water from pyridine, which potassium hydroxide was not capable of withdrawing. K. J. P. O.

Influence of Inactive Substances on the Optical Rotation of Dextrose. INA A. MILROY (*Zeit. physikal. Chem.*, 1904, **50**, 443—464).—The following substances, when added to an aqueous solution of dextrose, are found to increase the specific rotation, the dextrose solution being first kept for at least 24 hours after its preparation : phosphoric, arsenic, and boric acids, aluminium acetate, cerium sulphate, lead acetate, sodium tungstate, ammonium molybdate, methyl, ethyl, *n*-propyl, and *iso*propyl alcohols, acetone, acetaldehyde, and glycerol. In general, the increase of the specific rotation is approximately proportional to the amount of added substance. When methyl and ethyl alcohols are added, the rotation does not at once assume a steady value, but gradually increases with the time, becoming constant after 48—72 hours. In the case of *n*-propyl alcohol and acetone, the same phenomenon is observed only for the larger additions of these substances; when the added quantities are smaller, the rotation falls off with the time, finally reaching a constant value, which, however, is still greater than that for dextrose alone.

The following substances, added to dextrose solutions, diminish the specific rotation: potassium, sodium, and barium hydroxides, ethylamine, diethylamine, triethylamine, pyridine, borax, mercuric chloride, aniline hydrochloride, dimethylaniline hydrochloride, phenol, and pyrogallol. So far as the bases in this list are concerned, the diminution of rotation is more extensive and more rapid the stronger the base. It will be observed that in general the effect of acids is to increase, the effect of bases is to diminish, the rotation of dextrose.

The following substances are found to be without effect on the rotation : magnesium sulphate, ammonia alum, thorium, uranium and copper nitrates, and ferric chloride.

[Compare somewhat similar work on lactose, Trey, Abstr., 1904, i, 292.] J. C. P.

Cæsium Methylamide. ETIENNE RENGADE (*Compt. rend.*, 1905, **140**, 246—248).—Moissan has shown that cæsium reacts with ammonia at 40° to form cæsium-ammonium (compare Abstr., 1903, ii, 477), and the author finds that, although the metal dissolves in methylamine at $-20°$, the solution of cæsium-methylammonium thus obtained decomposes readily, giving off hydrogen and forming cæsium-methylamide, NHMeCs, in white, silky crystals, which decompose explosively on being rapidly heated or on contact with moist air ; at 115° to 120°, however, they are gradually decomposed with the formation of cæsium cyanide and the liberation of hydrogen, and they are slowly decomposed by water yielding methylamine and cæsium hydroxide. M. A. W.

Diaminoguanidine. GUIDO PELLIZZARI and C. CANTONI (*Ber.*, 1905, **38**, 283—284).—A claim for priority (compare Stollé and Hofmann, this vol., i, 28). W. A. D.

Condensation of some Esters with Ethyl Carbamate and with Ethyl Aminoacetate. OTTO DIELS and HANS HEINTZEL (*Ber.*, 1905, **38**, 297—305).—*Ethyl bromoacetylcarbamate*,

$$CH_2Br\cdot CO\cdot NH\cdot CO_2Et,$$

prepared by boiling an ethereal solution of ethyl bromoacetate and ethyl sodiocarbamate, $CHNa\cdot CO_2Et$, crystallises from dilute alcohol in long, slender needles and melts at 120—121°. *Ethyl α-bromopropionylcarbamate*, $CHMeBr\cdot CO\cdot NH\cdot CO_2Et$, prepared in similar manner from ethyl α-bromopropionate, crystallises from dilute alcohol or from ethyl acetate in short, thick prisms, sinters at 97°, and melts at 100—101°. *Ethyl α-bromobutyrylcarbamate* is similar and melts at 80—81°; *ethyl α-bromo*iso*butyrylcarbamate* melts at 63—64°. As the length of the carbon chain of the halogen acid increases, the ease of interaction with ethyl carbamate diminishes.

Ethyl cinnamoylcarbamate, $CHPh\colon CH\cdot CO\cdot NH\cdot CO_2Et$, prepared from ethyl cinnamate and ethyl carbamate, crystallises from a mixture of light petroleum and ethyl acetate in long needles, melts at 110—111°, and combines with bromine forming the *dibromide*,

$$CHPhBr\cdot CHBr\cdot CO\cdot NH\cdot CO_2Et,$$

which melts at 131—132°.

Ethyl sodiocarbamate simply eliminates 2HBr from two molecules of ethyl bromomalonate, giving rise to ethyl ethylenetetracarboxylate, $C(CO_2Et)_2\colon C(CO_2Et)_2$.

In presence of potassium hydroxide, ethyl aminoacetate combines with ethyl chloroacetate, alcohol being eliminated, to form *ethyl chloroacetylaminoacetate*, $CH_2Cl\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et$, which crystallises from a mixture of ethyl acetate and light petroleum in thin, rectangular plates and melts at 62—63°. *Ethyl cyanoacetylaminoacetate*, obtained in similar manner from ethyl cyanoacetate, crystallises from water and melts at 100—101°.

Ethyl aminoacetate combines with ethyl sodiocarbamate, alcohol being eliminated, to form ethyl hydantoate, which was not isolated, but characterised by its giving rise to hydantoin. W. A. D.

Internally Complex Metallic Salts. [Copper Glycine.] Heinrich Ley (*Zeit. Elektrochem.*, 1904, **10**, 954—956).—The molecular weight of copper glycine dissolved in water as determined by the freezing point method is almost normal, and its conductivity in aqueous solution is very small. It is therefore very little dissociated. The copper in this salt has been represented as replacing the hydrogen of the carboxyl groups or that of the amino-groups. The latter formula is doubtful, because diethylaminoacetic acid forms a salt which is quite analogous to the copper salt of glycine. The following experiments prove that the copper is linked to oxygen and not to nitrogen. When ammonia is added to a solution of copper glycine, no change in the deep blue colour of the solution takes place, but by determining the coefficient of partition of the ammonia between the solution and chloroform it is shown that the ammonia has combined with the salt. The combination might yield the salt $Cu(NH\cdot CH_2\cdot CO_2NH_4)_2$ or the complex cathion $[Cu(NH_3)_n]$ and the anion $NH_2\cdot CH_2\cdot CO_2$. An experiment showed that the blue colour moves toward the cathode when the solution is electrolysed, proving that the copper exists in the cathion. In order to explain the dark blue colour of the solutions, the author supposes that the salts are internally complex, the NH_2 groups playing

the same part as the NH_3 molecules attached to copper in the complex copper ammonia compounds. T. E.

Hydrolysis of Leucine Ethyl Ester by the Pancreatic Ferment. OTTO WARBURG (*Ber.*, 1905, 38, 187—188. Compare E. Fischer and Bergell, Abstr., 1903, i, 694; 1904, i, 867).—When the synthetical racemic ethyl ester of leucine is left in contact with water and crude pancreatin at the ordinary temperature, the *d*-ester is not hydrolysed, whereas the *l*-ester yields *l*-leucine. Fresh pancreas juice has the same effect. This affords a further example of "asymmetric hydrolysis." J. J. S.

Betaine Ethyl Ester Hydrochloride. ALBERT KOEPPEN (*Ber.* 1905, 38, 167—169).—*Betaine ethyl ester hydrochloride*, prepared by the action of 33 per cent. alcoholic solution of trimethylamine on ethyl chloroacetate, separates from ethyl alcohol in deliquescent crystals and melts at 143·5°. Its *platinichloride*, $(NMe_3{\cdot}CH_2{\cdot}CO_2Et)_2PtCl_6$, forms glistening, orange-coloured crystals. When boiled for two hours with hydrochloric acid, betaine ethyl ester hydrochloride forms betaine hydrochloride, which was identified by its crystalline form and by its platinichloride.

Betaine ethyl ester itself could not be prepared by the action of moist silver oxide on its hydrochloride. A. McK.

Formation of *C*-Acyl Derivatives from Ethyl Cyanoacetate by means of Pyridine and Quinoline. ARTHUR MICHAEL and O. ECKSTEIN (*Ber.*, 1905, 38, 50—53. Compare Dieckmann and Breest, Abstr., 1904, i, 845).—The experiments of Claisen and Haase (Abstr., 1900, i, 373) make it probable that the question whether an *O*- or a *C*-derivative is formed in the acylation of ethyl acetoacetate and similar compounds by the pyridine method depends on the stability of the primary additive product towards the base.

Ethyl cyanoacetoacetate, prepared by the action of acetyl chloride and pyridine on ethyl cyanoacetate in the cold, forms a *semicarbazone*, crystallising in colourless needles and melting at 190°.

When benzoyl chloride is added to a mixture of ethyl cyanoacetate and pyridine, even at a low temperature, a brown substance is produced. On replacing the pyridine by quinoline, however, ethyl cyanobenzoylacetate is obtained (compare Haller, Abstr., 1886, 240). A neutral *compound* containing nitrogen, but of unknown constitution, was also obtained, crystallising from dilute alcohol in almost colourless microscopic needles, melting at 178° and dissolving readily in organic solvents.

Ethyl ethylacetoacetate and ethyl methylacetoacetate do not yield acetyl derivatives with acetyl chloride and pyridine. C. H. D.

Supposed Existence of Thiocyanate of Iron and Probable Constitution of the Hæmoglobin of the Blood. NAZARENO TARUGI (*Gazzetta*, 1904, 34, ii, 326—348. Compare Abstr., 1903, ii, 460, and 1904, ii, 220; and Vitali, Abstr., 1904, ii, 104 and 600).—Free thiocyanic acid does not give van Deen's reaction, because this is

characteristic of the normal thiocyanogen group, while the free acid contains the *iso*-form, which, when introduced into a salt, is converted wholly or partially into the thiocyanogen group. The red coloration formed by the action of ferric chloride on a thiocyanate is due to the formation of the iron salt of a *peroxythiocyanic acid* according to the reversible equation: $12FeCl_3 + 6H_2O + 6KCNS \rightleftarrows 2FeHC_3N_3O_3S_3 + 6KCl + 10FeCl_2 + 10HCl$. The free acid, $C_3H_3O_3N_3S_3$, as well as all its acid salts, have a red colour. Solutions of oxalates, tartrates, &c., decolorise the acid and convert it into the corresponding normal salts, which are again decomposed by mineral acids with liberation of the peroxy-acid and formation of a red coloration. When a dilute solution of the free acid is heated, it becomes decolorised, and oxygen is liberated from the acid while the sulphur present is oxidised to sulphuric acid. With concentrated solutions, heating produces an increase in the depth of colour.

Peroxythiocyanic acid may also be prepared by the oxidation of thiocyanates in ethereal solution by means of nitric or chromic acid. The ethereal solution of the acid is decolorised by reducing agents.

The author expresses the structure of hæmoglobin as

$$(x)\cdot N_2C_2S_2\cdot Fe\cdot Fe\cdot N_2C_2S_2\cdot(x)$$

and that of oxyhæmoglobin as $(x)\cdot N_2C_2S_2O_2\cdot Fe\cdot Fe\cdot N_2C_2S_2O_2\cdot(x)$, where (x) represents an albumin group. T. H. P.

Two Complex Salts of Molybdenum. ALBERTO CHILESOTTI (*Gazzetta*, 1904, **34**, ii, 493—503).—The interaction of the double chloride of molybdenum and potassium (Abstr., 1903, ii, 730) with potassium thiocyanate yields a *thiocyanate* of *molybdenum* and *potassium*, $K_3Mo(CNS)_6,4H_2O$, which forms orange-coloured crystals readily soluble in water and readily loses water of crystallisation, becoming dark red, or, if completely dehydrated in a desiccator over phosphoric oxide or by heating, almost black in colour. In the neutral solution of the double salt, hydrogen peroxide produces a green coloration, which changes to blue and finally to yellow; hydrogen cyanide appears to be formed in this oxidation. Bromine added to an alkaline solution of the salt produces the same changes of colour. Lead acetate gives an orange-yellow precipitate insoluble in acetic acid, silver nitrate a flocculent yellow precipitate, and mercuric nitrate a brick-red precipitate, which becomes black on boiling the solution. Mercuric chloride yields a vivid red precipitate which turns yellow and has probably the composition $[Mo(SCN)_6]_2Hg_3$.

With potassium cyanide, the double chloride of potassium and molybdenum yields the *double cyanide*, $Mo(CN)_8K_4,2H_2O$, which forms yellow crystals, readily soluble in water, yielding a neutral solution. The solution is stable when kept away from strong light, but when exposed to the direct action of the sun's rays, its colour changes almost instantaneously to red and then to pale green, hydrogen cyanide being simultaneously formed. That the formula of the salt is that given above, and not a multiple of it, is shown by conductivity determinations. Even in extremely dilute solution, ferric chloride is coloured an intense blue by solutions of the double cyanide. Solutions of silver and mercurous salts give voluminous, pale yellow precipitates

insoluble in dilute acids. This double cyanide presents the first known case of a complex ion which is stable in solution and which contains a metal combined with eight halogenic residues. T. H. P.

Condensation of Natural Leucine and Carbamic Acid. LOUIS HUGOUNENQ and ALBERT MOREL (*Compt. rend.*, 1905, **140**, 150—151).—iso*Butylhydantoic acid*, $NH_2\cdot CO\cdot NH\cdot CH(CH_2Pr^{\beta})\cdot CO_2H$, obtained by dissolving leucine in excess of carbamide at 130—135°, crystallises in very white needles decomposing at 200—210°, is slightly soluble in cold, readily so in boiling water or alcohol, insoluble in mineral acids, but dissolves in acetic acid, forms soluble salts with the alkali metals, and is decomposed by sodium hypobromite forming leucic acid. iso*Butylhydantoin*, $CO<\begin{matrix}NH\cdot CH\cdot CH_2Pr^{\beta}\\ NH\cdot \overset{|}{C}O\end{matrix}$, obtained by heating *iso*butylhydantoic acid at 150°, crystallises in silky needles melting at 200—210°, is slightly soluble in cold water, readily soluble in cold alcohol, insoluble in mineral acids, but soluble in alkalis owing to the acid nature of the hydrogen atom of the imino-group situated between two carbonyls; it is not acted on by sodium hypobromite, and on prolonged boiling with water it is converted into *iso*butylhydantoic acid. M. A. W.

Cyanodialkylacetylcarbamides. FIRMA EMANUEL MERCK (D.R.-P. 156383. Compare this vol., ii, 179).—When the esters of dialkylcyanoacetic acids react with carbamide or its alkyl derivatives in the presence of a metallic ethoxide at the ordinary temperature, cyanodialkylacetylcarbamides are formed, which condense on heating to form iminodialkylbarbituric acids. Thiocarbamide or guanidine may also be employed in place of carbamide.

α-Cyano-α-ethylbutyrylcarbamide, $CN\cdot CEt_2\cdot CO\cdot NH\cdot CO\cdot NH_2$, from ethyl α-cyano-α-ethylbutyrate, carbamide, and sodium ethoxide, crystallises from hot water, melts at 118°, and dissolves in alcohol, ether, or ethyl acetate. *Cyanoethylbutyrylthiocarbamide* forms slender, yellow needles and melts and decomposes at 261°. *Cyanoethylbutyrylguanidine* dissolves readily in water. *α-Cyano-α-propylvalerylcarbamide* crystallises from alcohol in colourless prisms and melts at 101°. *Cyanoethylbutyrylphenylcarbamide*, from ethyl cyanoethylbutyrate and phenylcarbamide, forms long, flat prisms and melts at 156°. C. H. D.

Preparation, Use, and Recovery of Semicarbazide. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1905, [iii], **33**, 162—165).—Details are given of a method of preparing semicarbazide, which is a slight modification of that used by Thiele and Stange (Abstr., 1894, i, 165). In the preparation of semicarbazones, the authors dissolve free semicarbazide in as little water as possible, add to the solution a few drops of acetic acid, and finally the aldehyde or ketone and sufficient methyl or ethyl alcohol to give a clear solution, which is finally warmed on the water-bath for 15 minutes. This process gives better results than the use of semicarbazide hydrochloride in combination with sodium acetate.

In regenerating a ketone or aldehyde from its semicarbazone, the latter is boiled for one hour in a reflux apparatus with a slight excess of dilute sulphuric acid (15 per cent.), and the aldehyde or ketone finally distilled off in a current of steam. The residue contains hydrazine sulphate and semicarbazide sulphate. On concentration and cooling, the former crystallises out from the mother liquor; after neutralisation with potassium carbonate and concentration under reduced pressure, two-thirds of the hydrazine initially used may be recovered as the sulphate by extraction with alcohol. T. A. H.

Imino-*CC*-dialkylbarbituric Acids. Firma Emanuel Merck (D.R.-P. 156384. Compare Abstr., 1903, i, 799; 1904, i, 380; this vol., i, 178).—Carbamide reacts with the esters of dialkylcyanoacetic acids on warming with sodium ethoxide in alcoholic solution on the water-bath, forming iminodialkylbarbituric acids, $CRR' {<}^{C(NH)\cdot NH}_{CO\text{——}NH}{>} CO$, from which the corresponding dialkylbarbituric acids are readily obtained by heating with dilute acids.

Iminodiethylbarbituric acid, from carbamide and ethyl cyanoethylbutyrate, melts and decomposes at 195° and dissolves in 136 parts of water at 20° and in 23·5 parts at 100°. *Iminodipropylbarbituric acid* melts and decomposes at 305°; *iminodibenzylbarbituric acid* crystallises from hot alcohol; *iminoethylpropylbarbituric acid* melts at 302°. C. H. D.

Preparation of Barbituric Acid and its Homologues. Firma Emanuel Merck (D.R.-P. 156385. Compare preceding abstract).—Dilute acids hydrolyse the alkyl derivatives of iminobarbituric acid on heating, yielding alkylated barbituric acids.

Dipropylbarbituric acid melts at 146°; *dibenzylbarbituric acid* melts at 222°; *propylbarbituric acid* (from *iminopropylbarbituric acid* melting at about 300°) melts at 207°; *ethylpropylbarbituric acid* forms large, colourless needles and melts at 145°. C. H. D.

Nitriles of Hydroxy- and Amino-carboxylic Acids. Emil Knoevenagel (*Ber.*, 1905, **38**, 213—217. Compare Trans., 1904, i, 981, 989, 994, 1024, 1027, 1028).—Polemical. A reply to Bucherer's criticisms (this vol., i, 59). J. J. S.

Copper Double Cyanides. Hermann Grossmann and Peter von der Forst (*Zeit. anorg. Chem.*, 1905, **43**, 94—110. Compare Abstr., 1904, i, 983).—The *sodium* salt, $NaCu_2(CN)_3,2H_2O$, prepared by the action of cuprous cyanide on a concentrated solution of sodium cyanide, forms glistening, monoclinic crystals. The *ammonium* salt, $NH_4Cu_2(CN)_3,H_2O$, forms prismatic needles. The *lithium* salt,

$$LiCu_2(CN)_3,3H_2O,$$

forms prismatic needles. These three salts are readily decomposed by water.

The *rubidium* salt, $Rb_2Cu_3(CN)_5$, crystallises in octahedral leaflets. The *cæsium* salt, $Cs_2Cu_3(CN)_5$, separates in tetragonal or hexagonal

cubes. The *calcium* salt, $CaCu_3(CN)_5$, forms rhombic, prismatic needles.

The *ammonium* salt, $NH_4Cu(CN)_2$, prepared by careful evaporation at 70° of the liquid from which the salt $NH_4Cu_2(CN)_3,H_2O$ has been removed, separates in nacreous leaflets. The *rubidium* salt, $RbCu(CN)_2$, prepared by the interaction of rubidium carbonate, cuprous cyanide, and hydrocyanic acid, forms rhombic plates. The *cæsium* salt,

$$CsCu(CN)_2,1\tfrac{1}{2}H_2O,$$

forms glistening needles. The *barium* salt, $BaCu_2(CN)_4,4H_2O$, crystallises in plates and in rhombic pyramids. The *strontium* salt,

$$SrCu(CN)_4,8H_2O,$$

forms monoclinic plates. The *magnesium* salt, $MgCu_2(CN)_4,11H_2O$, separates in monoclinic needles.

The *cæsium* salt, $Cs_2Cu(CN)_3,H_2O$, crystallises in leaflets. The *barium* salt, $BaCu_2(CN)_3,3H_2O$, forms prismatic needles. The *calcium* salt, $CaCu(CN)_3,4H_2O$, forms prismatic needles. The authors have obtained these salts from mother liquors from which other salts had been removed.

From determinations of the lowering of freezing point, the conclusion is drawn that the salt $K_3Cu(CN)_4$ undergoes hydrolytic dissociation in very dilute solution.

The *sodium* salt, $Na_3Cu(CN)_4,3H_2O$, forms hygroscopic, hexagonal leaflets. Its electrolytic conductivity was measured.

Crystallographic measurements of most of the salts examined are given. A. McK.

Derivatives of Formhydroxamic Acid and the Possible Existence of Esters of Fulminic Acid. Henry C. Biddle (*Amer. Chem. J.*, 1905, **33**, 60—68).—Attempts have been made to prepare benzyl fulminate and the corresponding benzoyl and acetyl derivatives by the elimination of hydrogen chloride from the benzyl, benzoyl, and acetyl derivatives of chloro-formoxime (Abstr., 1900, i, 137), but without success.

Methyl formhydroxamate, $COH\cdot NH\cdot OMe$, prepared by the action of formic acid on α-methylhydroxylamine, is a colourless liquid, which boils at 116—117° under 33 mm., at 123—124° under 45 mm., and at 126—127° under 50 mm. pressure; it solidifies in colourless prisms and melts at 38—39°. The ester is deliquescent and is decomposed by hydrochloric acid with formation of formic acid and α-methylhydroxylamine hydrochloride. When treated with solution of platinic chloride, the ester undergoes dissociation, and the platinichloride of α-methylhydroxylamine is produced. The *silver* salt of methyl formhydroxamate forms white leaflets and reacts with acetyl and benzoyl chlorides and with methyl and ethyl iodides with formation of the corresponding acyl and alkyl derivatives. When molecular proportions of methyl formhydroxamate and phenylcarbimide are warmed together, an additive *compound* is produced, which crystallises in colourless leaflets, melts at 123—123·5°, and is readily soluble in chloroform and sparingly so in ether, alcohol, or hot water.

By the action of phosphorus pentachloride on methyl formhydroxamate, *methyl chloroformoxime*, $CHCl{:}N\cdot OMe$, is produced as a

volatile liquid, which boils at 68°, has an odour like that of chloroform, and is slightly soluble in water. When this substance is treated with potassium hydroxide, small quantities of a neutral unsaturated *compound* are produced, which has a strong odour resembling that of *iso*nitriles, boils at about 50—60°, and is probably methyl fulminate, $C{\vdots}N{\cdot}OMe$, but has not yet been isolated in sufficient quantity to admit of its identification. Methyl fulminate also appears to be formed by the interaction of α-methylhydroxylamine hydrochloride, chloroform, and alcoholic potassium hydroxide, the same *iso*nitrile-like odour being produced. E. G.

Nitrimines and Nitriminic Acids. Roland Scholl (*Annalen*, 1905, **338**, 1—35).—The ketoximes of the fatty series are converted by nitrous acid or nitrogen peroxide into ψ-nitroles, but in the case of the oximes of pinacolin, camphor, camphenone, fenchone, menthone, tanacetone, mesityl oxide, and santonin, the oxime group is exchanged for the group N_2O_2. This reaction is confined to ketoximes in which the group $>C{:}N{\cdot}OH$ is linked to a tertiary or quaternary carbon atom. The group, $C_2HN_2O_2$, which is produced in this reaction must either have the constitution $>C{:}\overset{|}{C}{\cdot}NH{\cdot}NO_2$, an enylnitroamine, or $>CH{\cdot}\overset{|}{C}{:}N{\cdot}NO_2$, a nitroimine. Since the compounds do not react with phenylcarbimide and diazomethane, the latter formula is the more probable.

The nitroimines are ψ-acids and yield a series of salts which correspond with an acid of the formula $>C{:}\overset{|}{C}{\cdot}N{:}NO{\cdot}OH$ or

$$>C{:}\overset{|}{C}{\cdot}N{<}\begin{matrix}N{\cdot}OH\\ |\\ O\end{matrix}\ .$$

When the acid is set free from its salts, it is immediately reconverted into the nitroimine, but, since the salts yield the two series of alkyl derivatives, $>C{:}\overset{|}{C}{\cdot}N{<}\begin{matrix}N{\cdot}OR\\ |\\ O\end{matrix}$ and $>C{:}\overset{|}{C}{\cdot}NR{\cdot}NO_2$, it is probable that an enylnitroamine is intermediarily produced in the conversion.

Of the two possible constitutions of the group present in the salts $N_2O{\cdot}OH$, the expression, $N{<}\begin{matrix}N{\cdot}OH\\ |\\ O\end{matrix}$, is preferred, since it represents more simply the cleavage of the mesitylnitroiminic acid into nitrous acid and α-mesityloxime, and at the same time the formation of nitroimines from oximes and nitrous acid. Only those oximes are capable of undergoing this reaction which have a loosely bound hydrogen atom on the β-carbon atom relatively to the oxime group, thus:

$$>CH{\cdot}\overset{|}{C}{:}N{\cdot}OH.$$

This hydrogen atom, together with the hydrogen atom of the oxime group, combines with the oxygen of the nitrous acid in the condensation; a group $>\begin{matrix}C\text{———}\\ |\\ -C{:}N{\cdot}O\end{matrix}{>}N{\cdot}OH$ is thus formed, which then, by re-arrangement, passes into the group $>C{:}\overset{|}{C}{\cdot}N{<}\begin{matrix}N{\cdot}OH\\ |\\ O\end{matrix}$.

[With A. O. Weil and K. Holdermann.]—Pinacolinoxime on

treatment with phosphorus pentachloride in dry ether is converted into *acetyl*-tert.-*butylamide*, $CMe_3 \cdot NHAc$, which crystallises in needles, melts at 95°, sublimes very readily and boils at 194°; its *hydrochloride* formed from the ethereal solution is very hygroscopic. From this transformation, it follows that the oxime has the anti-configuration, $\begin{matrix} Me \cdot C \cdot CMe_3 \\ \| \\ N \cdot OH \end{matrix}$. Pinacolinoxime reacts with phenylcarbamide, yielding the *compound* $C_6H_{12}\colon NO \cdot CO \cdot NHPh$, which crystallises in needles melting at 131·5°. The *acetyl* derivative of the oxime, $C_6H_{12}\colon N \cdot OAc$, is an oil boiling at 83—84° under 10 mm., at 100—101° under 25 mm., and at 208—210° under the atmospheric pressure.

Pinacolin-nitroimine, $CMe_3 \cdot CMe\colon N \cdot NO_2$, is prepared by dissolving pinacolinoxime in ether and adding nitrogen peroxide, and by fractionating the product after removal of the acid by water and alkali. It boils at 80·5—81°, and is always mixed with oxime and methyl-*tert.*-butyldinitromethane, $CMe_3 \cdot CMe(NO_2)_2$, which separates as a crystalline hydrochloride when the nitroimine is dissolved in concentrated hydrochloric acid; it forms very volatile crystals smelling of camphor, melts at 173—174°, and boils at 101—103° under 34 mm. pressure. The salts of the nitroimine are formed when it is heated with concentrated alkali hydroxides, but the ammonium salt is not produced by passing dry ammonia into a solution in anhydrous ether. It is oxidised by permanganate and reduces ammoniacal silver solutions. It does not react with diazomethane or phenylcarbimide, and, when distilled under the ordinary pressure, decomposes into pinacolin. On bromination, it yields dibromopinacolin, $C_6H_{10}OBr_2$ (m. p. 74·5°), which is identical with the substance obtained from δδ-dibromo-ββ-dimethyl-γ-butanone. On reduction with aluminium amalgam in moist ether, the nitroimine is converted into the oxime.

The *sodium* salt, obtained from the nitroimine by the use of sodium ethoxide, crystallises in silky, hygroscopic needles, which are hydrolysed in aqueous solution; the *potassium* salt forms hygroscopic needles, and the *silver* salt, a greyish-white precipitate. When the sodium salt is heated in methyl-alcoholic solution with methyl iodide for 2 hours, a N-*methyl* derivative, $CMe_3 \cdot C(CH_2) \cdot NMe \cdot NO_2$, is obtained in the form of volatile crystals melting at 39° and decomposed by hydrochloric acid, methylamine being produced; it is not oxidised by permanganate. The corresponding *ethyl*, iso*propyl* and n-*butyl* derivatives, are oily liquids of peculiar odour. The O-*methyl* ester,

$$CMe_3 \cdot C(CH_2) \cdot N{<}\begin{matrix} N \cdot OMe \\ | \\ O \end{matrix},$$

is prepared from the silver salt and methyl iodide at a low temperature in ethereal solution; it is an oil which is readily oxidised by alkaline permanganate and decomposed by hydriodic acid, methyl iodide being formed. The corresponding ethyl ester is a yellow oil. The nitroimine also yields a series of *N*-acyl derivatives when the sodium salt is treated with acyl chlorides in hot anhydrous alcohol; the *acetyl*, *benzoyl*, and *benzenesulphonic* compounds were all thus prepared, and formed oils which are not decomposed by water.

K. J. P. O.

Platinum Phosphorus Halogen Compounds and their Derivatives. II. ARTHUR ROSENHEIM and WALTER LEVY (*Zeit. anorg. Chem.*, 1905, **43**, 34—47. Compare Abstr., 1904, ii, 131).—By the action of organic amines on alkyl phosphite-platochlorides, two series of isomeric compounds, $RNH_2PtCl_2P(OR')_3$, are produced. The stable series probably corresponds with platosoammine chloride and the labile with platosemidiammine chloride.

When aniline is gradually added to a solution of ethyl phosphite-platochloride, $[P(OEt)_3,PtCl_2]_2$, in alcohol or benzene at 0°, crystals of the *yellow* compound, $PtPCl_2,C_{12}H_{12}O_3N$, first separate, whilst from the filtrate silky needles of a colourless *compound*, isomeric with the former, separate. The relative proportion of those compounds produced is dependent on the temperature conditions, the latter being formed in larger amount the higher the temperature. The yellow compound is the labile form; at its melting point, 108°, it is transformed into the white variety, which melts at 147°. The transformation is also effected on exposure at the ordinary temperature or on rubbing with a glass rod. The yellow form is probably *cis*-triethyl phosphite-anilineplatochloride, $\left[{}^{Cl}_{Cl}Pt^{P(OEt)_3}_{NH_2Ph}\right]$, whilst the white compound is probably *trans*-triethyl phosphite-anilineplatochloride,

$$\left[{}^{P(OEt)_3}_{Cl}Pt^{Cl}_{NH_2Ph}\right].$$

The analogous *pyridine* compounds, $PtPCl_2,C_{11}H_{20}O_3N$, were prepared. The two isomerides were crystalline and resembled the corresponding aniline compounds.

The action of ammonia was different from that of the organic bases. When a current of dry ammonia was passed into a solution of triethyl phosphite-platochloride in benzene, voluminous white crystals of the *compound* $[Pt(NH_3)_2P(OEt)_3]_2Cl_4$ separated. It is a good electrolyte as distinct from the compounds with aniline and pyridine described. With chloroplatinic acid, it forms the *platinichloride*, $[Pt(NH_3)_2P(OEt)_3]PtCl_6$.

The action of ammonia on methyl diphosphite-platochloride is analogous, white crystals of the *compound* $[Pt(NH_3)_2(P[OMe]_3)_2]Cl_2$, being produced.

Phenyl diphosphite-platochloride, $[PtCl_2(P[OPh]_3)_2]$, separates from alcohol in white crystals and melts at 155°.

The platinum phosphorus bromo-compounds described behave similarly to the corresponding chloro-compounds.

Phosphorus bromide-platobromide, $[PtBr_2(PBr_3)]_2$, prepared by the action of phosphorus pentabromide on platinum black, forms reddish-brown crystals which, by an excess of phosphorus tribromide, are converted into *diphosphorus bromide-platobromide*, $[PtBr_2(PBr_3)_2]$, which is readily acted on by moisture and reacts violently with methyl alcohol to form the *ester*, $[PtBr_2(P[OMe]_3)_2]$, which melts at 136°. When ethyl alcohol is used instead of methyl alcohol in the latter reaction, the reaction proceeds normally, triethyl phosphite-platobromide, $[P(OEt)_3,PtBr_2]_2$, being produced. By the action of aniline on the latter compound, two isomerides are formed, as in the case of the action on the corresponding chloro-compound.

The *compound* $[PtBr_4(OP[OEt]_3)_2]$ melts at 155°. A. McK.

Primary Arsines. William M. Dehn (*Amer. Chem. J.*, 1905, 33, 101—153. Compare Palmer and Dehn, Abstr., 1902, i, 86).—Primary arsines can be readily prepared by the reduction of alkylarsonic acids with amalgamated zinc dust and hydrochloric acid.

A detailed account is given of the method of preparation of methylarsine. Methylarsine is soluble in water to the extent of 85 parts per million. On oxidation with nitric acid, it is converted into arsenic oxide and methylarsonic acid. When the compound is passed into a neutral or alkaline solution of silver nitrate, silver is precipitated and methylarsonic acid is produced. If the gas is led into a solution of bromine in carbon disulphide, arsenic tribromide is formed. The arsine reacts with solution of iodine with formation of methylarsonic and hydriodic acids, $AsH_2Me + 6I + 3H_2O = AsMeO(OH)_2 + 6HI$ When methylarsine is treated with dry hydrogen chloride or hydrogen sulphide, little or no action takes place. The compound is not affected by yellow phosphorus either at the ordinary temperature or at 100°. It is decomposed by aqueous mercuric chloride with formation of mercurous chloride and mercury methylarsonate. When methylarsine is heated with excess of methyl iodide for 8 hours in a sealed tube at 110°, tetramethylarsonium iodide is produced; with ethyl iodide, under similar conditions, methyltriethylarsonium iodide is formed.

Magnesium ethylarsonate, $MgAsEtO_3$, may be prepared in the following manner. A solution of potassium arsenite is treated with ethyl iodide, and when the reaction is complete the solution is acidified with dilute hydrochloric acid and filtered. Chlorine is passed into the filtrate, the iodine is removed by filtration, the solution is rendered alkaline with ammonia, treated with a large excess of magnesia mixture, and left for 24 hours. The liquid is filtered, and, on evaporation, magnesium ethylarsonate separates. When dried at 140°, magnesium methylarsonate is obtained as a white powder, readily soluble in acids but insoluble in alkalis. It is soluble in water at 22° to the extent of 2·31 parts per 1000, and in 10 per cent. solution of ammonium chloride to the extent of 2·66 parts per 1000. At 25°, 0·125 gram dissolves in 1 litre of alcohol. The salt usually contains $1H_2O$, which is not completely removed at 145°. When hydrogen sulphide is passed into a solution of magnesium ethylarsonate in hydrochloric acid, *ethylarsine disulphide*, $AsEtS_2$, is obtained as a viscid, yellow oil having a peculiar, disagreeable odour; it has a sp. gr. 1·836 at 24°, is easily soluble in benzene, chloroform, or carbon disulphide, and insoluble in water, alcohol, or ether, and is dissolved by dilute nitric acid with formation of ethylarsonic acid.

Trimethylarsine sulphide, Me_3AsS, obtained by the action of heat on methylarsine disulphide, crystallises in white, tough, lustrous needles and melts at 174°. Triethylarsine sulphide melts at 119·5° and reacts with hydrobromic acid with formation of triethylarsine dibromide and hydrogen sulphide.

Magnesium methylarsonate forms small, white crystals and is soluble in water to the extent of 2·118 grams per litre at 22° and 3·085 grams at 99°.

Silver phenylarsonate, Ag_2PhAsO_3, is obtained as a white, glistening

precipitate when silver nitrate is added to an ammoniacal solution of phenylarsonic acid; it is practically insoluble in water.

A series of experiments was carried out with the object of ascertaining the best conditions for the preparation of alkylarsonic acids by G. Meyer's reaction (Abstr., 1883, 1078). The results showed that a better yield is obtained with potassium arsenite than with the sodium salt, that ethyl iodide gives a better result than the bromide, and that in the aliphatic series the yields are inversely as the molecular weight of the alkyl haloid employed.

Ethylarsine, AsH_2Et, is a liquid which resembles methylarsine, boils at 36°, has a sp. gr. 1·217 at 22°, is soluble in water to the extent of 126 parts per million at 19°, and has an extremely disagreeable, penetrating odour. It combines with oxygen with formation of ethylarsine oxide and water, is oxidised by concentrated nitric acid to ethylarsonic acid, arsenic oxide, and acetic acid, and when passed into silver nitrate solution is converted into ethylarsonic acid, silver being precipitated. When the arsine is led into concentrated sulphuric acid, white crystals are obtained which probably consist of the *salt*, $2AsH_2Et,H_2SO_4$. By the action of ethyl iodide on ethylarsine at 110°, tetraethylarsonium iodide is produced. *Trimethylethylarsonium iodide* forms hard, glistening needles, softens at about 300°, and shrinks at 320°, and is soluble in water, chloroform, or hot alcohol. *Ethyltri*iso*amylarsonium iodide* forms compact crystals, does not melt below 250°, is soluble in alcohol, and sparingly so in chloroform. When ethylarsine is heated with carbon disulphide for 10 hours in a sealed tube at 120°, triethylarsine sulphide is produced, together with small quantities of an oil with an irritating odour resembling that of cacodyl.

Phenylarsine boils at 93° under 70 mm., 84° under 50 mm, and at 77° under 33 mm. pressure, and is soluble in alcohol, ether, or carbon disulphide, but insoluble in water. When it is treated with bromine, a brick-red precipitate is produced which probably consists of the *substance* $AsHPhBr,HBr$; on exposure to the air, it becomes liquid and evolves hydrogen bromide, and by the action of zinc and hydrochloric acid is converted into phenylarsine. Phenylarsine decolorises solution of iodine with formation of phenylarsonic acid and other products. When the arsine is heated with excess of ethyl iodide for 6 hours at 120°, phenyltriethylarsonium iodide is produced. Phenyltrimethylarsonium iodide can be prepared in a similar manner. *Phenyltri*iso*amylarsonium iodide* forms pearly-white crystals, melts at 163°, and is very soluble in chloroform or alcohol, but insoluble in benzene or cold water. When phenylarsine was heated with phenyl iodide, no arsonium iodide could be obtained. E. G.

Spatial Formula for Benzene. BERTHOLD KÖNIG (*Chem. Zeit.*, 1905, **29**, 30).—The author suggests a "cube" formula for benzene, in which the six carbon atoms are arranged in six of the corners of a cube in such a manner that each carbon atom is united by one bond to one hydrogen atom, by two bonds, one to each of the two neighbouring carbon atoms, whilst the fourth bond extends to one of the two remaining corners of the cube which are not occupied by carbon atoms. The three bonds which extend to each of those two corners are supposed to mutually satisfy one another.

In substitution compounds of benzene, this formula is transformed into a plane hexagonal type. A. McK.

Hydrolysis of Methyl Benzenesulphonate. ARTHUR PRAETORIUS (*Monatsh.*, 1905, **26**, 1—34. Compare Wegscheider, Abstr., 1902, ii, 493; Wegscheider and Furcht, Abstr., 1903, i, 342).—The hydrolysis of methyl benzenesulphonate with water is a unimolecular reaction, and the rate of hydrolysis, therefore, is proportional to the concentration of the ester. As the hydrolysis constant with 0·05375 *N*-sulphuric acid, *K* 0·0007175, is little greater than that with water, *K* 0·0007015, the hydrolysis in aqueous solution cannot be accelerated by the presence of hydrogen ions. The formula for the alkaline hydrolysis of carboxylic esters is not applicable to sulphonic esters, as in the hydrolysis of methyl benzenesulphonate with an alkali the action of the water cannot be neglected; it must be replaced by Wegscheider's formula (*loc. cit.*). G. Y.

Triphenylmethyl. PAUL JACOBSON (*Ber.*, 1905, **38**, 196—199. Compare Tschitschibabin. This vol., i, 125).—The author agrees with Tschitschibabin that Ullmann and Borsum's hexaphenylethane is most probably benzhydryltetraphenylmethane, but is of opinion that Gomberg's triphenylmethyl should not be represented as hexaphenylethane, but rather as 4-*triphenylmethyl*-1-*diphenylmethylene*-cyclo-$\Delta^{2,5}$-*hexadiene*, $CPh_2{:}C{<}^{CH:CH}_{CH:CH}{>}CH{\cdot}\vdots CPh_3$.

Such a formula accounts for the bimolecular nature of triphenylmethyl and at the same time, by a rupture at the dotted line, indicates how the compound could readily react as free triphenylmethyl.

It also accounts for the transformation of Gomberg's compound into Ullmann and Borsum's so-called hexaphenylethane by the wandering of a single hydrogen atom. J. J. S.

Condensation of Benzaldehyde with Toluene. ALFRED KLIEGL. (*Ber.*, 1905, **38**, 84—87).—Griepentrog found (Abstr., 1886, 887) that benzaldehyde and toluene condense together in the presence of zinc chloride, but was unable to obtain a crystalline product. Benzaldehyde does not condense with benzene in presence of concentrated sulphuric acid, but toluene condenses slowly in the cold. After removal of unaltered benzaldehyde and toluene, the product is extracted with ether and finally distilled by means of superheated steam. *Phenyldi*-p-*tolylmethane* crystallises from methyl alcohol and melts at 54—54·5°. Crystallisation only takes place slowly, as the compound tends to separate in an oily state, and inoculation with a crystal is necessary.

Phenyldi-p-*tolylcarbinol*, prepared by the addition of methyl benzoate and magnesium to an ethereal solution of *p*-bromotoluene, separates on cooling its solution in light petroleum in a freezing mixture in large, colourless crystals, sintering at 75° and melting at 76·5—77·5°. Its solution in glacial acetic acid gives a yellowish-green coloration with concentrated sulphuric acid. Zinc dust and acetic acid reduce it to phenyldi-*p*-tolylmethane, identical with that just described.

C. H. D.

Phenylfluorene. ALFRED KLIEGL (*Ber.*, 1905, 38, 284—297).—Phenylfluorene, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>CHPh$, is best prepared by distilling triphenylcarbinol with crystalline phosphoric acid. Phenylfluorenol, obtained by Ullmann and von Wurstemberger's method (Abstr., 1904, i, 154), crystallises from carbon tetrachloride with $\frac{1}{2}CCl_4$, and melts, when free from solvent, at 107—107·5°. Bromine at the ordinary temperature (1 mol.) converts phenylfluorene dissolved in carbon disulphide into 9-*bromo*-9-*phenylfluorene*, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>CBrPh$, which crystallises from light petroleum in slender needles and melts at 99°; on treating the bromo-compound with hot methyl alcohol, the *methyl* ether, $C_{19}H_{13}\cdot OMe$, is obtained in long prisms melting at 92·5—93°; the *ethyl* ether, $C_{19}H_{13}\cdot OEt$, obtained in similar manner, crystallises in small prisms and melts at 113°. Bromophenylfluorene is very stable towards boiling water and alkalis, but is converted into phenylfluorenol by heating with hydrated sodium acetate in glacial acetic acid solution. The *acetyl* derivative of phenylfluorenol separates from acetic acid or alcohol in prismatic crystals and melts at 169—169·5°. Hydroxydiphenylfluorene, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>CPh\cdot C_6H_4\cdot OH$, prepared by condensing phenylfluorenol with phenol, crystallises from 96 per cent. alcohol in needles containing alcohol, or from acetic acid, and melts at 189·5—190°; the *acetyl* derivative, $C_{19}H_{13}\cdot C_6H_4\cdot OAc$, crystallises from acetic acid or alcohol in slender needles and melts at 176°. *Diphenylfluorene ether*, $C_{38}H_{26}O$, prepared by adding concentrated sulphuric acid to phenylfluorenol dissolved in glacial acetic acid, is sparingly soluble in all solvents save chloroform and decomposes between 320 and 360°.

9-*Chloro*-9-*phenylfluorene*, $C_{19}H_{13}Cl$, prepared by the action of phosphorus pentachloride on phenylfluorenol in benzene solution, crystallises from light petroleum, melts at 78—79°, and with aniline gives *anilinophenylfluorene*, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>CPh\cdot NHPh$, crystallising from light petroleum or alcohol and melting at 175°.

Phenylbenzylfluorene, $C_{26}H_{20}$, prepared by heating phenylfluorene with benzyl chloride and solid potassium hydroxide for 6 hours at 230°, crystallises from a mixture of glacial acetic acid and light petroleum and melts at 136—137°.

On nitration in cold glacial acetic acid solution, phenylfluorene gives rise to 2-*nitro*-9-*phenylfluorene*, $\begin{matrix} NO_2\cdot C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>CHPh$, which crystallises from glacial acetic acid in leaflets and melts at 135°; when the hydrocarbon is added to an excess of nitric acid of sp. gr. 1·52, *tetranitrophenylfluorene*, is obtained, which melts and decomposes at about 235°. 2-Nitro-9-phenylfluorene, on oxidation with chromic acid in acetic acid solution, gives 4-*nitro*-2-*benzoylbenzoic acid*, $CO_2H\cdot C_6H_3(NO_2)\cdot COPh$, which crystallises from benzene or water, melts at 161·5—162°, and gives a *methyl* ester crystallising in prisms and melting at 104·5°. 2-*Nitroanthraquinone*, formed on heating 4-nitro-2-benzoylbenzoic acid with concentrated sulphuric acid at 100°, crystallises from light petroleum

in mossy aggregates of needles, melts at 180·5—181°, and is easily reduced by alkaline stannous chloride solution to 2-aminoanthraquinone. 4-*Amino-2-benzoylbenzoic acid*, prepared by the reduction of the corresponding nitro-compound with ammoniacal ferrous hydroxide, crystallises from alcohol in golden-yellow, efflorescent prisms with 1EtOH, and melts at 195°; 4-*hydroxy-2-benzoylbenzoic acid*, prepared by means of the diazo-reaction, decomposes at about 220—222° and is resolved by fusion with sodium hydroxide into benzoic and *p*-hydroxybenzoic acids. W. A. D.

Syntheses in the Anthracene Series. III. 9 : 9 : 10 : 10-Tetraphenyldihydroanthracene and its Derivatives. ALBIN HALLER and ALFRED GUYOT (*Compt. rend.*, 1905, **140**, 283—287. Compare Abstr., 1904, i, 660).—When 9-hydroxy-9 : 10 : 10-triphenyldihydroanthracene is heated in glacial acetic acid solution with phenol, aniline, dimethyl- or diethyl-aniline, condensation takes place and mono-substituted derivatives of 9 : 9 : 10 : 10-tetraphenyldihydroanthracene are formed in almost quantitative yield. When phenol is employed, the addition of a small quantity of sulphuric acid is necessary for the reaction to take place. The general formula of the products is

$$C_6H_4<\begin{matrix}CPh_2\text{———}\\CPh(C_6H_4R)\end{matrix}>C_6H_4,$$

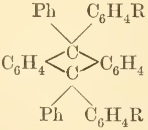
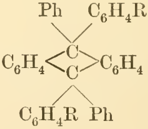
where R represents either, OH, NH_2, NMe_2, or NEt_2.

The *hydroxy*-derivative crystallises in small prisms melting at about 308°. It is insoluble in alkalis, but dissolves very readily in alcoholic potash.

The *amino*-derivative forms small, white crystals melting at 320°. When diazotised and treated with β-naphthol, a red colouring matter is obtained. When the diazo-compound is boiled with absolute alcohol, there is no formation of hydrocarbon, but the *ethoxy*-derivative is obtained in small, white crystals melting at 265°. These crystals are only slightly soluble in the ordinary solvents. The *dimethylamino*-derivative forms small, white crystals melting at 285°. The *diethylamino*-derivative forms colourless needles melting at 216°.

9 : 10-Dihydroxy-9 : 10-diphenyldihydroanthracene condenses in a similar manner with dimethyl- and diethyl-anilines.

In each case, equal quantities of two isomerides are obtained, which can be very easily separated by reason of their great difference in solubility. They are evidently the *cis-* and *trans-* forms corresponding with

 and 

H. M. D.

9 : 10-Diphenylphenanthrene. HEINRICH BILTZ (*Ber.*, 1905, **38**, 203—206. Compare Abstr., 1893, i, 718; 1897, i, 533).—The compound melting at 235° (corr.) which was previously obtained by

condensing benzene and chloral in the presence of aluminium chloride is identical with Werner and Grob's 9 : 10-diphenylphenanthrene (Abstr., 1904, i, 864). The same compound is obtained by the action of aluminium chloride on a benzene solution of tetraphenylethylene. The reaction is thus similar to the formation of phenylfluorene from triphenylmethane. J. J. S.

Action of Ammonium Nitrite and Ammonium Nitrate (or of Nascent Nitrogen and Nitrous Oxide) on Aromatic Compounds. WILHELM VAUBEL (*Chem. Zeit.*, 1904, **28**, 1245—1246).—The action of ammonium nitrite on aniline, *m*-phenylenediamine, sodium aminonaphthalenesulphonate, dimethylaniline, phenol, and benzaldehyde respectively, and of ammonium nitrate on naphthalene, anthracene, phenol, resorcinol, aniline, *o*-toluidine, *p*-toluidine, benzidine, *m*-phenylenediamine, *p*-phenylenediamine, diphenylamine, dimethylaniline, α- and β-ethylnaphthylamines, benzaldehyde, and benzoic acid respectively was examined. By the action of ammonium nitrite in aqueous solution at 60—70° on phenols, nitroso-compounds or their decomposition products are formed. By the action of ammonium nitrite on amines, diazo-compounds or their decomposition products are formed. Ammonium nitrate had often an oxidising action in the cases examined; aniline and other amines were oxidised. In other cases, by the action of ammonium nitrate, nitrogen was introduced into certain of the compounds investigated, as, for example, with phenol, naphthalene, benzaldehyde, and benzoic acid, oxidation proceeding at the same time. A. McK.

Introduction of the Groups $\cdot CH_2\cdot OH$ and $\cdot CH_2\cdot$ into Primary Aromatic Amines and Preparation of Compounds of an Imidic Character. E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 1303—1311).—The action of formaldehyde solution on the sodium derivative of formanilide yields a yellow *oil*, $C_6H_4<\begin{matrix}N\cdot CH_2\cdot OH\\ | \\ CH_2\end{matrix}$, which decomposes on distillation. When treated with dilute hydrochloric, nitric, or sulphuric acid, the oil congeals to an orange-coloured *base* having the composition $\left[OH\cdot CH_2\cdot C_6H_3<\begin{matrix}NH\\ | \\ CH_2\end{matrix}\right]_n$, which is soluble in acids, has a high molecular weight and, when treated with sodium nitrite in acid solution, gives a *nitroso*-compound,

$$\left[OH\cdot CH_2\cdot C_6H_3<\begin{matrix}N\cdot NO\\ | \\ CH_2\end{matrix}\right]_n.$$

When boiled with an alkaline solution of β-naphthol, this nitrosocompound is converted into a red *azo-dye*, $ONa\cdot C_{10}H_6\cdot N\colon N\cdot C_6H_3(CH_2\cdot OH)_2$. With mercuric iodide dissolved in potassium iodide, mercuric cyanide dissolved in potassium or ammonium cyanide, or mercuric chloride, an acid solution of the base yields a yellow, powdery precipitate, which in the last case has the composition $O\left(CH_2\cdot C_6H_3<\begin{matrix}NH\\ | \\ CH_2\end{matrix}\right)_2,HgCl_2$. The *precipitate* obtained with gold chloride has the formula C_7H_7NAu.

The action of formaldehyde on the sodium derivative of formyl-β-

naphthylamine yields an *oil*, $C_{10}H_6<\overset{CH_2}{\underset{N\cdot CH_2\cdot OH}{|}}$, which is converted by hydrochloric acid into an orange-coloured, pasty mass, precipitable from concentrated hydrochloric acid by water as a yellow *powder* having the composition $OH\cdot CH_2\cdot C_{10}H_5<\overset{NH}{\underset{CH_2}{|}}$. With sodium nitrite, an acid solution of this base yields a slightly soluble *nitroso*-compound, $OH\cdot CH_2\cdot C_{10}H_5<\overset{N\cdot NO}{\underset{CH_2}{|}}$, which gives a red *pigment* with alkaline β-naphthol solution. With mercuric salts, the base yields insoluble, yellow compounds, whilst aqueous ferric chloride oxidises the base in acid solution to a brown powder. Auric chloride precipitates a yellow powder which becomes brown on heating.

The action of formaldehyde solution on the sodium derivative of the anilide of sulphanilic acid yields the *base* $SO_3H\cdot C_6H_3<\overset{NH}{\underset{CH_2}{|}}$.

The sodium derivative of formanilide reacts also with acetaldehyde giving the *imine base*, $C_6H_4<\overset{NH(1)}{\underset{CHMe(4)}{|}}$, and with acetone giving the *base*, $C_6H_4<\overset{NH(1)}{\underset{CMe_2(4)}{|}}$. Like other iminic bases these give yellow precipitates with mercuric chloride, mercuric iodide in potassium iodide solution, platinic chloride, or auric chloride. With nitrous acid, they give the corresponding *nitroso*-compounds,

$$C_6H_4<\overset{N\cdot NO}{\underset{CHMe}{|}} \quad \text{and} \quad C_6H_4<\overset{N\cdot NO}{\underset{CMe_2}{|}}.$$

T. H. P.

Replacement of the Aldehyde Oxygen Atom by Two Univalent Hydrocarbon Radicles by means of Grignard's Reaction. Franz Sachs and Ludwig Sachs (*Ber.*, 1905, **38**, 517—526).—*p*-iso*Propyldimethylaniline*, $NMe_2\cdot C_6H_4Pr^{\beta}$, is formed when *p*-dimethylaminophenylmethylcarbinol is heated with an excess of magnesium methyl iodide at 100°, or when 1 mol. of *p*-dimethylaminobenzaldehyde is added to magnesium and methyl bromide, corresponding with at least 2 mols. of magnesium methyl bromide in absolute ethereal solution, the ether distilled off, and the residue heated at 100° for 6—8 hours. It is a colourless oil with an aromatic odour, boils at 235·6° (corr.) under 752 mm. pressure, is volatile in a current of steam, and has a sp. gr. 0·92286 at 18°/18° and n_D 1·5353 at 18°. The *methiodide*, $C_{12}H_{20}NI$, crystallises in glistening leaflets, melts at 198° (corr.), and, when treated with silver oxide in boiling aqueous solution, yields the strongly alkaline ammonium base, which crystallises in yellow leaflets and melts at 93—94°; the *ethobromide* crystallises in broad rose-coloured leaflets and melts at 66—67°; the *hydrochloride*, $C_{11}H_{17}N,HCl$, crystallises in broad, glistening leaflets and melts at 155°; the *platinichloride*, $(C_{11}H_{17}N)_2,H_2PtCl_6$, crystallises in large, golden-brown needles, blackens at about 197°, and melts and decomposes at 207—208° (corr.); the *aurichloride* crystallises in long, lemon-yellow needles or broad leaflets and melts at 95°.

4-*Dimethylamino*-1-*a-ethylpropylbenzene*, $NMe_2 \cdot C_6H_4 \cdot CHEt_2$, formed in the same manner from *p*-dimethylaminobenzaldehyde and magnesium ethyl bromide, is a yellow oil which boils at 127—129° under 7 mm., at 262·2° (corr.) under 754 mm. pressure, is volatile in a current of steam, and has a sp. gr. 0·91425 at 19°/19° and n_D 1·5266 at 19°. The *methiodide*, $C_{14}H_{24}NI$, crystallises in large, silky leaflets and melts at 168—169°; the *hydrochloride*, $C_{13}H_{21}N,HCl$ crystallises in large, glistening leaflets and melts at 131°; the *platinichloride*,

$$(C_{13}H_{21}N)_2H_2PtCl_6,$$

crystallises in yellow needles and melts and decomposes at 195° (corr.).

p-Dimethylaminotriphenylmethane, $NMe_2 \cdot C_6H_4 \cdot CHPh_2$, is prepared in the same manner by the action of *p*-dimethylaminobenzaldehyde on magnesium phenyl bromide.

4-*Diethylamino*-1-*a-ethylpropylbenzene*, $NEt_2 \cdot C_6H_4 \cdot CHEt_2$, prepared in the same manner by the action of *p*-diethylaminobenzaldehyde on magnesium and ethyl bromide, is obtained as an oil which boils at 140—141° under 7 mm., or at 278° (corr.) under 760·5 mm. pressure, and has a sp. gr. 0·90584 at 21°/21°, n_D 1·5209 at 21°.

The *hydrochloride* forms a strongly hygroscopic syrup; the *platinichloride* forms golden, prismatic crystals and decomposes at 179° (corr.); the *methiodide* is an oil.

p-*Dimethylaminobenzylidenesemicarbazone*,

$$NMe_2 \cdot C_6H_4 \cdot CH{:}N \cdot NH \cdot CO \cdot NH_2,$$

crystallises in yellow leaflets and melts and decomposes at 224° (corr.). p-*Dimethylaminothiobenzamide*, $NMe_2 \cdot C_6H_4 \cdot CS \cdot NH_2$, formed by the action of hydrogen sulphide on *p*-dimethylaminobenzonitrile dissolved in alcoholic ammonia, crystallises in yellow needles, sinters at 170°, and melts and decomposes at 209° (corr.). p-*Diethylaminobenzylidenesemicarbazone*, $NEt_2 \cdot C_6H_4 \cdot CH{:}N \cdot NH \cdot CO \cdot NH_2$, crystallises in glistening, yellow scales and melts and decomposes at 214° (corr.). p-*Diethylaminobenzylideneaniline*, $NEt_2 \cdot C_6H_4 \cdot CH{:}NPh$, crystallises in large, glistening, yellow scales and melts at 108—109°. G. Y.

Giustiniani's Benzylmalimide. Oskar Lutz (*J. pr. Chem.*, 1905, [ii], 71, 34—38. Compare Abstr., 1904, i, 831; Giustiniani, Abstr., 1892, 820; Ladenburg and Hertz, Abstr., 1897, i, 460).—Polemical. A reply to Ladenburg and Herz (Abstr., 1904, i, 992). G. Y.

4 : 4′-Diaminoformyl- (acetyl) -diphenylamine. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 156388).—4 : 4′-*Dinitroformyldiphenylamine*, $COH \cdot N(C_6H_4 \cdot NO_2)_2$, prepared by nitrating formyldiphenylamine in concentrated sulphuric acid solution, separates from hot formic acid in small crystals and melts at 159°. This and the corresponding acetyl compound are reduced by iron and a small quantity of sulphuric acid, the bases formed being extracted with dilute sulphuric acid and precipitated by addition of sodium acetate. The sulphates, unlike that of 4 : 4′-diaminodiphenylamine, dissolve readily in water.

4 : 4′-*Diaminoformyldiphenylamine*, $COH \cdot N(C_6H_4 \cdot NH_2)_2$, separates from alcohol in small crystals and melts at 193°; 4 : 4′-*diaminoacetyldiphenylamine* melts at 195°. The bases yield tetrazonium compounds, from which azo-dyes may be prepared. C. H. D.

Stereochemical Studies. I. New Method of Separating Racemic Compounds. Emil Erlenmeyer, jun., and Alfred Arnold (*Annalen*, 1904, **337**, 307—328).—After a *résumé* of the methods at present in use for separating racemic compounds into their active components, Pasteur's use of an active base (or acid) to separate a racemic acid (or base) is discussed. In this case, two semi-racemic salts, + + and − +, are formed, which can generally be separated by considerable difference in solubility. Such semiracemic compounds should also be formed in other reactions between a racemic and an active substance, for example, between hydrocyanic acid and active aldehydes. In this case, the racemic carbon atom is produced in the reaction. Representing the two linkings of the carbonyl group by *a* and *b* respectively, thus:

$$(+R)\cdot CH\overset{a}{\underset{b}{<\!\!>}}O \rightarrow (+R)\cdot CH\overset{a}{\underset{b}{<}}{}^{CN}_{OH} \text{ and } (+R)\cdot CH\overset{a}{\underset{b}{<}}{}^{OH}_{CN},$$

a semiracemic compound is formed which can be separated into its constituents by taking advantage of different solubilities, &c. If R is symmetric, as in benzaldehyde, equal numbers of + and − molecules are produced. If R is asymmetric, different numbers of + and − molecules are produced, as, for example, in the reduction of *d*-benzoin, where the carbonyl group becomes reduced, only hydrobenzoin and no *iso*hydrobenzoin is formed, hence a selective reduction of one only of the links of the group occurs.

On applying these views to the separating of racemic bases into their active constituents, it was found possible to obtain the + and − forms of *iso*diphenylhydroxyethylamine by causing it to react with the active aldehyde, helicin, and separating the two condensation products by their different solubilities.

The hydrochloride of the *d*-base melts at 228° and has $[\alpha]_D$ 80·23°; the hydrochloride of the *l*-base has the same melting point, and both are more easily soluble in methyl alcohol than the *r*-salt. In addition to the tartrates of the *d*- and *l*-bases previously described, the neutral tartrate of the *r*-base, melting at 212—214°, has been isolated.

On fractionally evaporating the alcoholic solutions of the *r*-base and helicin under reduced pressure, crystals of the base

$$OH\cdot CHPh\cdot CHPh\cdot N\colon CH\cdot C_6H_4\cdot O\cdot C_6H_{11}O_5,$$

separate; this is the compound of helicin and the *d*-base, the corresponding compound of helicin and the *l*-base being deposited as an amorphous mass from the mother liquor. The derivative of the *d*-base crystallises in colourless needles melting at 189°, and has $[\alpha]_D$ − 6·43°, whilst the derivative of the *l*-base melts at 90°, is hygroscopic, and has $[\alpha]_D$ − 43·6°. The active bases were obtained by hydrolysing these compounds with dilute hydrochloric acid. The *d*-base crystallised in needles melting at 113—114°, and had $[\alpha]_D$ − 109·72°, whilst the *l*-base formed crystals melting at 114°, was slightly less soluble than the *d*-base, and had $[\alpha]_D$ − 108°. The solubility of the *r*-base in alcohol was only one-third of that of the active bases.

K. J. P. O.

New Isomerism of Ethylene Derivatives. EMIL ERLENMEYER, jun., and ALFRED ARNOLD (*Annalen*, 1904, **337**, 329—353. Compare preceding abstract).—In substances of the type $CR_1R_2{:}CR_1R_3$, which can exist in two geometric isomerides, transformation of the labile into the stable form can undoubtedly occur directly, by a simple revolution of the linking between the carbon atoms and without any addition to the ethylene linkage. It can be shown that in this revolution, there are two intermediate positions, in which the attractive forces causing the revolution are in equilibrium; these two positions must therefore have the same stability. Further, it can be shown that these two positions bear to one another the relation of object to image if the four groups R_1,R_2, R_1,R_3 are supposed to occupy the four angles of a tetrahedra.

Applying these considerations to the isomerism of the cinnamic acids, it is suggested that *allo*cinnamic acid, which crystallises in hemihedric forms, is a racemic compound of the two stereoisomerides. Possibly Liebermann's *iso*cinnamic acid is one of these isomerides, whilst Erlenmeyer's *iso*cinnamic acid is the geometric isomeride of ordinary cinnamic acid.

It is doubtful whether these stereoisomerides would be optically active, but their asymmetry would have an effect when they were combined with an asymmetric substance. Such an example appears to exist in the compounds of *iso*diphenylhydroxyethylamine and cinnamaldehyde. Since isomeric compounds appear to be formed from cinnamaldehyde and hippuric acid, it is possible that the aldehyde is itself composite. Cinnamaldehyde and *l*-*iso*diphenylhydroxyethylamine yield two isomeric dextrorotatory compounds, whilst the *d*-base yields another pair of lævorotatory compounds, five modifications with the inactive form altogether existing.

r-*iso*Diphenylhydroxyethylamine and cinnamaldehyde, when mixed in mol. proportions in alcoholic solution, yield a precipitate of the compound $OH{\cdot}CHPh{\cdot}CHPh{\cdot}N{:}CH{\cdot}CH{:}CHPh$, which forms colourless crystals melting and decomposing at 185°; it is decomposed into its constituents by dilute sulphuric acid. The *l*-base gives a similar substance, representing 50 per cent. of the material used; it is sparingly soluble, melts and decomposes at 190°, and is dextrorotatory; from the mother liquor, an isomeric substance is obtained which forms pale yellow crystals melting at 131° and having $[\alpha]_D+52{\cdot}56°$ in alcoholic solution. The *d*-base yields a similar pair of substances of similar properties, but lævorotatory, $[\alpha]_D-52{\cdot}12°$ in alcoholic solution. The solubility of the three substances of higher melting point in 100 parts of alcohol are, compound from *r*-base (m. p. 185°) 0·12 part, compound from *d*-base (m. p. 190°) 0·174 part, and compound from *l*-base (m. p. 190°) 0·178 part.

Derivatives of Racemic and Optically Active iso*Diphenylhydroxylethylamine.*—The benzylidene *compound* of the *d*-base, prepared from the components in alcoholic solution, crystallises in colourless needles melting at 137° and having $[\alpha]_D+55{\cdot}53°$ in alcohol solution; the benzylidene *compound* of the *l*-base melted at 137° and had $[\alpha]_D-56{\cdot}00°$. The *compound* from salicylaldehyde and the *r*-base forms pale yellow crystals melting at 113°. The anisaldehyde *compound* of the

r-base crystallises in colourless needles melting at 145°, the vanillin *compound* forms yellow, cubical crystals melting at 148°, the piperonal *compound* colourless needles melting at 131°, and the *p*-nitrobenzaldehyde *compound* yellow needles melting at 132°. Ethyl acetoacetate condenses with the *r*-base, forming yellow, rhombic crystals melting at 145°; the similar *compound* from pyruvic acid and the *r*-base forms crystals melting and decomposing at 152°; the analogous *compound* with the *d*-base is insoluble, melts at 161°, and has $[\alpha]_D + 88{\cdot}82°$ in alcoholic solution, whilst the derivative of the *l*-base, which melts at 161°, has $[\alpha]_D - 87{\cdot}71°$. The *acetyl* derivative of the *r*-base crystallises in colourless needles melting at 152°, and yields a *hydrochloride* melting at 193°; no diacetyl derivative could be obtained. The d-*acetyl* derivative melts at 159°, has $[\alpha]_D + 12{\cdot}74°$, and forms a *hydrochloride* melting at 196—197°. The l-*acetyl* derivative has $[\alpha]_D - 12{\cdot}80°$. The r-*benzoyl* derivative, prepared by the action of benzoyl chloride in benzene solution, crystallises in needles melting at 223°; the d-*benzoyl* derivative forms needles melting at 215° and having $[\alpha]_D + 29{\cdot}02°$ in methyl-alcoholic solution, and the l-*benzoyl* derivative melting at 214—215°, $[\alpha]_D - 29{\cdot}00°$. The r-*dibenzoyl* derivative, prepared by boiling the base with benzoyl chloride, is a powder melting at 187° and is identical with the compound obtained from diphenylhydroxyethylamine, a fact which shows that the latter changes partly into the *iso*-compound on benzoylating.

The hydrochloride of the *r*-base yields with potassium cyanate the *compound* $OH{\cdot}CHPh{\cdot}CHPh{\cdot}NH{\cdot}CO{\cdot}NH_2$, which separates from acetone in crystals containing acetone, and melts when dry at 157°.

K. J. P. O.

Action of Phosphorus Pentachloride on Tertiary Cyclic Amines. Synthesis of Dyes and Formation of Phosphorus. Paul Lemoult (*Compt. rend.*, 1905, **140**, 248—250. Compare Abstr., 1904, i, 380, 806, 807; this vol., i, 48).—Phosphorus pentachloride yields a deep blue coloration with dimethylaniline (compare Michler and Walden, Abstr., 1882, 175), which disappears on boiling, methyl chloride being evolved; if, however, the temperature is maintained at 80° to 100°, there is no evolution of gas, and the solid product, which is deeply coloured, consists of (1) tetramethyldiaminodiphenylmethane; (2) hexamethyltriaminotriphenylmethane, the leuco-base of hexamethylviolet; (3) the *compound* $PO(C_6H_4{\cdot}NMe_2)_3$, not yet described, but which gives with alcohol the compound $PO(C_6H_4{\cdot}NMe_2)_3,EtOH$, obtained by Michaelis and von Soden (Abstr., 1885, 1134); and (4) an orange-yellow substance containing free phosphorus. Colouring matters were also obtained when methylethylaniline, dimethyl-*o*-toluidine, benzylmethylaniline, or diphenylmethylamine replace the dimethylamine in the above reaction, but dimethyl-*p*-toluidine, diethylaniline, or benzylethylaniline do not give coloured products with phosphorus pentachloride. These facts show that only those tertiary cyclic amines in which the para-position of the aryl radicle is free and which contain at least one methyl group are capable of giving synthetical dyes with phosphorus pentachloride.

M. A. W.

Phenylcarbimide as a Reagent for Determining the Constitution of Tautomeric Compounds. Arthur Michael (*Ber.*, 1905, 38, 22—49. Compare Dieckmann, Hoppe, and Stein, this vol., i, 135).—The author has studied the action of phenylcarbimide on compounds showing enol-keto-tautomerism and their sodium derivatives, with a view to determining the influence of the more or less acid character of the compounds concerned on the course of the reaction. In the case of sodium derivatives, phenylcarbimide forms an additive product whenever the nature of the parent compound is such that the sodium is "more fully neutralised" in the additive product than in the original compound (Abstr., 1900, i, 321; 1904, ii, 164). When this is not the case, polymerisation to triphenyl *iso*cyanurate (Hofmann, *Ber.*, 1870, 3, 268) takes place, often accompanied by secondary decompositions.

Thus sodium ethoxide and the sodium derivatives of ethyl α-formylpropionate, formylcamphor, and ethyl formylphenylacetate only cause polymerisation of the phenylcarbimide, phenylurethane being also formed under certain conditions.

Phenylcarbimide reacts with the sodium or copper derivative of ethyl acetoacetate in ether at the ordinary temperature to form a C-*additive compound*, ONa·CMe⁚C(CO_2Et)·CO·NHPh. Acids set free the hydroxylic compound, crystallising from alcohol in large prisms and melting at 57° (compare Dieckmann, Abstr., 1900, i, 482). The *semicarbazone* melts at 152—154° and is converted into a *compound* melting at 210—220° by crystallisation from water. Potassium hydroxide hydrolyses it to the monoanilide of malonic acid.

Ethyl sodiomalonate and phenylcarbimide react vigorously in ether to form a C-*compound*, $C_{14}H_{17}O_5N$, crystallising from alcohol in long, white, prismatic needles and melting at 126°. The *sodium* salt is hydrolysed by water, and dissolves only in an excess of sodium hydroxide.

Ethyl sodiobenzoylacetate yields an additive compound, $C_{18}H_{17}O_4N$, crystallising in white, prismatic needles melting at 145—146°, but previously softening. This compound is neutral, but dissolves in alkali hydroxides on heating, and acids then precipitate the white, labile enolic form, which dissolves readily in alkaline solutions, but passes gradually into the stable ketonic form (compare Wislicenus, Abstr., 1899, i, 60; Ruhemann and Watson, Trans., 1904, 85, 456).

Sodiodiacetylmethane yields an *additive compound*, $C_{12}H_{13}O_3N$, crystallising from water in prismatic needles melting at 118—120°. It dissolves readily in alkali carbonates and is reprecipitated by acids. The enolic form has no tendency to ketonise. Alkali hydroxide decomposes it, forming acetoacetanilide.

Ethyl sodioformylacetate yields an *enolic additive compound*, OH·CH⁚C(CO_2Et)·CO·NHPh, crystallising from alcohol in white prisms melting at 52—53°. The *sodium* salt, $C_{12}H_{12}O_4NNa,2H_2O$, forms white crystals, moderately soluble in water. The *phenylhydrazone* forms white prisms melting at 136—137°.

In the reaction between ethyl sodioethylmalonate and phenylcarbimide, one carbethoxy-group is eliminated, and a *compound*,

$C_{25}H_{21}O_4N_3$, is formed, crystallising from benzene in rounded groups of small prisms melting at 141—142° and behaving as a weak monobasic acid. The *silver* salt forms white, prismatic needles. The same compound is obtained from ethyl ethylacetoacetate and phenylcarbimide. The *product* from ethyl sodiomethylmalonate melts at 198—200°.

Sodionitromethane and phenylcarbimide react together only slowly, forming *nitroacetanilide*, $NO_2 \cdot CH_2 \cdot CO \cdot NHPh$, crystallising from water in bright yellow, feathery leaflets melting at 138—139° and dissolving readily in alcohol, ether, chloroform, or benzene, together with *nitromalonanilide*, $NO_2 \cdot CH(CO \cdot NHPh)_2$, crystallising from alcohol in pale yellow leaflets melting at 141—142°.

Potassium nitroform does not react with phenylcarbimide.

The conclusion drawn by Goldschmidt and Meissler (Abstr., 1890, 499) that only enolic compounds form additive products on heating with phenylcarbimide is not justified. Acetophenone, ethyl malonate, ethyl ethylmalonate, and ethyl oxaloacetate do not react with phenylcarbimide at 100°. Ethyl ethylacetoacetate reacts at 180°, forming an oil boiling at 190—210° under 17 mm. pressure. In the series of compounds next examined, the reaction takes place more readily with increasing acidity of the compound employed. An accumulation of ketonic groups hinders the reaction, even when an enolic group is present.

Ethyl acetoacetate, diacetylmethane, and ethyl benzoylacetate yield the same additive products as their sodium derivatives. Dibenzoylmethane reacts with phenylcarbimide in ethereal solution at the ordinary temperature, the product melting at 195—196° or 205—207°, according to the time of heating (compare Wislicenus, *loc. cit.*).

Ethyl α-formylpropionate reacts readily to form the *compound* $CHO \cdot CMe(CO_2Et) \cdot CO \cdot NHPh$, crystallising from benzene in colourless, glistening, prismatic needles melting at 117—119°. It is insoluble in alkali hydroxides, but is slowly decomposed by them, forming *α-formylpropionanilide*, $C_{10}H_{11}O_2N$, melting at 82—87°. Semicarbazide acetate reacts with it to form a crystalline *compound* of unknown constitution, melting at 231—232°.

Both ethyl α- and β-formylphenylacetates react readily with phenylcarbimide, the products melting at 59° and 116° respectively. This result is contrary to the statement of W. Wislicenus (Abstr., 1896, i, 552), and is being further investigated.

Nitroethane and nitromethane do not react below 140°, great decomposition then taking place.

Dibenzoylacetylmethane and its enolic isomeride do not yield additive products with phenylcarbimide. The former yields a *compound* melting at 118—122° and not containing nitrogen. Enolic benzoyldiacetylmethane yields a *compound* containing nitrogen, which is being further investigated.

Phloroglucinol and phenylcarbimide react in cold ethereal solution to form a *compound* $C_{27}H_{21}O_6N_3$, crystallising from alcohol or benzene in white, prismatic needles melting at 190—192°, and isomeric with the compound obtained by Goldschmidt and Meissler (Abstr., 1890, 499). C. H. D.

Thymomenthol [Hexahydrothymol] and its Derivatives. Léon Brunel (*Compt. rend.*, 1905, **140**, 252—253).—Hexahydrothymol (for which the author suggests the name thymomenthol to recall its origin and its close relationship to menthol) is more conveniently prepared by the direct hydrogenation of thymol in the presence of reduced nickel at 160° than at 180—185° (compare Abstr., 1904, i, 158), the amount of acetone formed (compare Sabatier and Senderens, Abstr., 1903, i, 454) being much less at the lower temperature. Pure thymomenthol is a syrupy, colourless liquid with a strong odour of mint, has a sp. gr. 0·913 at 0°, melts between −5° and 0°, boils at 215·5° under atmospheric pressure, is insoluble in water, readily soluble in alcohol, ether, or acetic acid, volatilises rapidly at the ordinary temperature, and is converted into *tetrahydrocymene* (thymomenthene) by the action of phosphoric oxide or potassium hydrogen sulphate; the new hydrocarbon closely resembles menthene, having a sp. gr. 0·823 at 0° and boiling at 167—168°, whilst the corresponding values for menthene are 0·8266 and 167·4°. The esters of thymomenthol are readily prepared by heating the alcohol with excess of the acid anhydride, or by heating molecular proportions of the alcohol and acid anhydride with pyridine, or by the action of the acid anhydride on the sodium derivative of the alcohol; they yield on hydrolysis β-thymomenthol, which is a stereoisomeride of the original or α-compound, and crystallises in long, colourless needles melting at 28° and boiling at 217° under atmospheric pressure, is readily soluble in alcohol, ether, acetone, light petroleum, or acetic acid, insoluble in water, and is much less volatile than the α-isomeride. *β-Thymomenthyl hydrogen succinate*, $CO_2H{\cdot}C_2H_4{\cdot}CO_2{\cdot}C_{10}H_{19}$, crystallises in thin, colourless, odourless needles melting at 80°, soluble in alcohol and in warm light petroleum. *β-Thymomenthyl hydrogen phthalate*, $CO_2H{\cdot}C_6H_4{\cdot}CO_2{\cdot}C_{10}H_{19}$, crystallises in large, colourless, odourless prisms melting at 128°, readily soluble in alcohol or chloroform.

M. A. W.

Nitrosophenol Dyes. III. Herman Decker and Boris Solonina (*Ber.*, 1905, **38**, 64—68; 720. Compare Abstr., 1902, i, 767; 1903, i, 838).—When crude nitric acid is added to a solution of thymol methyl ether in acetic acid, a dark blue, uncrystallisable solution of an oxonium salt is obtained (compare Kehrmann, Abstr., 1902, i, 767). On reducing at 0° with stannous chloride and hydrochloric acid and decomposing the stannochloride formed, *dithymolylamine dimethyl ether*, $NH(C_6H_2MePr{\cdot}OMe)_2$, is obtained, melting at 88·5—89° after crystallisation from alcohol. The *hydrochloride* forms white needles, commencing to melt at 140°; the *hydriodide* forms white needles melting indistinctly at 136°. Ferric chloride oxidises the ether in alcoholic solution to *thymoquinonethymolylimide methyl ether*,

$$O{:}C_6H_2MePr{:}N{\cdot}C_6H_2MePr{\cdot}OMe,$$

crystallising from methyl alcohol in red needles and melting at 66—67°. Stannous chloride reduces it quantitatively to *dithymolylamine methyl ether*. The same red indophenol ether may be prepared by the action of nitroso-sulphuric acid on thymol and methylation of the product by means of methyl sulphate.

Thymol *n*-butyl ether and nitric acid react in acetic acid solution to form an *oxonium dinitrate* containing the complex

$$C_4H_9\cdot O\cdot C_{10}H_{12}\cdot N\colon C_{10}H_{12}\colon O(C_4H_9)\cdot NO_3,$$

the other NO_3 group being probably attached to the nitrogen atom. The salt forms bronze crystals melting at 66°, and is more stable than the ethyl derivative obtained by Kehrmann. *Dithymolylamine dibutyl ether*, $C_{28}H_{43}O_2N$, forms bright yellow crystals melting at 69·5°; the *hydrochloride* forms white needles and melts at 107°. *Thymoquinone-thymolylimide* n-*butyl ether*, $C_{24}H_{33}O_2N$, crystallises in red prisms and melts at 55°.

The same colour-reactions (formation of blue oxonium salt and red indophenol ether) were observed in the case of thymol *iso*propyl ether and *p*-xylenol ethyl and methyl ethers. C. H. D.

Myristicin. I. ENRICO RIMINI (*Gazzetta*, 1904, **34**, ii, 281—300).—In order to ascertain whether Angeli's method of detecting the presence of an allyl group by the action of nitrous acid is of general applicability, the author has tested it on a number of compounds. It is found that nitrous acid reacts with all compounds containing an allyl group as a side-chain, but with much greater difficulty than with those having a propenyl side group. The reaction can, however, be employed to distinguish allyl compounds from propenyl compounds, since the nitrosites obtained yield, in the former case, nitro-oximes, and in the latter peroxides of dioximes. From the behaviour of myristicin and *iso*myristicin towards nitrous acid and towards mercuric acetate, it is concluded that the former contains an allyl side-chain and the latter a propenyl side-chain.

Methylchavicol α-nitrosite, $OMe\cdot C_6H_4\cdot C_3H_5,N_2O_3$, prepared by the action of nitrous acid on methylchavicol in light petroleum solution, forms a pale lemon-yellow powder melting and decomposing at 147°. On boiling with absolute alcohol in a reflux apparatus until dissolved, it passes into *methylchavicol β-nitrosite*,

$$OMe\cdot C_6H_4\cdot CH_2\cdot C(NOH)\cdot CH_2\cdot NO_2,$$

which is deposited from benzene in white crystals melting at 112°.

p-*Methoxyphenylnitroacetone*, $OMe\cdot C_6H_4\cdot CH_2\cdot CO\cdot CH_2\cdot NO_2$, obtained by boiling the preceding compound with dilute sulphuric acid, crystallises from alcohol in shining, white scales melting at 89°. On oxidation with dilute alkaline permanganate solution, it yields anisic and homoanisic acids. On gentle reduction with stannous chloride and hydrochloric acid in alcoholic solution, it gives p-*methoxyphenyl-aminoacetone hydrochloride*, $OMe\cdot C_6H_4\cdot CH_2\cdot CO\cdot CH_2\cdot NH_2,HCl$, which crystallises from alcohol in shining, white laminæ melting and decomposing at 198—199°. The corresponding *picrate*,

$$C_{10}H_{13}O_2N,OH\cdot C_6H_2(NO_2)_3,$$

crystallises from alcohol in orange-yellow needles decomposing at 148°.

2 : 5-*Di*-p-*anisylpyrazine*,

$$OMe\cdot C_6H_4\cdot CH_2\cdot C{<}{\substack{CH\colon N\\ N\cdot CH}}{>}C\cdot CH_2\cdot C_6H_4\cdot OMe,$$

prepared by the action of ammonia on *p*-methoxyphenylaminoacetone

hydrochloride, is deposited from aqueous alcohol as a white, crystalline powder melting and decomposing at about 150°.

Methyleugenol a-nitrosite, $C_6H_3(OMe)_2 \cdot C_3H_5,N_2O_3$, which is only obtainable with difficulty, forms a lemon-yellow powder, melting and decomposing at 130°. When boiled with alcohol, a syrupy β-nitrosite is formed, and this, with dilute sulphuric acid, gives *dimethoxyphenylnitroacetone*, $C_6H_3(OMe)_2 \cdot CH_2 \cdot CO \cdot CH_2 \cdot NO_2$, which crystallises from alcohol in plates melting at 103°. On treatment with hydroxylamine in presence of sodium carbonate and hydroxide, this does not give the nitroxime expected, but *dimethoxybenzyloxamic acid*,

$$C_6H_3(OMe)_2 \cdot CH_2 \cdot CO \cdot NH \cdot OH,$$

which separates from alcohol in mammillary aggregates melting and decomposing at 137°, and gives a violet coloration with ferric chloride and a bottle-green precipitate with copper acetate.

When reduced, dimethoxyphenylnitroacetone yields *dimethoxyphenylaminoacetone*, the *picrate* of which,

$$C_6H_3(OMe)_2 \cdot CH_2 \cdot CO \cdot CH_2 \cdot NH_2, C_6H_2(NO_2)_3 \cdot OH,$$

separates from alcohol in crystals melting and decomposing at 153°.

Apiole a-nitrosite, $CH_2{:}O_2{:}C_6H(OMe)_2 \cdot C_3H_5,N_2O_3$, prepared only with great difficulty and in small yield, is a lemon-yellow powder, which melts and decomposes at about 138° and is insoluble in all ordinary solvents. *Dill-apiole a-nitrosite* melts and decomposes at 139°.

Myristicin a-nitrosite, $CH_2{:}O_2{:}C_6H_2(OMe) \cdot C_3H_5,N_2O_3$, formed, together with a large proportion of resin, from myristicin and nitrous acid, is a yellow powder melting and decomposing at 130°. The β-nitrosite could only be obtained as a syrup, which, when treated with dilute sulphuric acid, yields *methoxymethylenedioxyphenylnitroacetone*, $CH_2{:}O_2{:}C_6H_2(OMe) \cdot CH_2 \cdot CO \cdot CH_2 \cdot NO_2$, crystallising from alcohol in shining scales melting at 132—133°.

On reduction, the foregoing compound yields *methoxymethylenedioxyphenylaminoacetone*, the *picrate* of which,

$$CH_2{:}O_2{:}C_6H_2(OMe) \cdot CH_2 \cdot CO \cdot CH_2 \cdot NH_2, C_6H_3O_7N_3,$$

separates from alcohol in crystals melting and evolving gas at 182°.

*Di*iso*nitroso*iso*myristicin peroxide*,

$$CH_2{:}O_2{:}C_6H_2(OMe) \cdot C \lessgtr \begin{matrix} CMe \\ NO- \end{matrix} \gt NO,$$

prepared by the action of nitrous acid on *iso*myristicin, is deposited from alcohol in shining, yellow crystals melting at 103°. Reduction by means of zinc dust and acetic acid in alcoholic solution yields *di*iso*nitroso*iso*myristicin*, $CH_2{:}O_2{:}C_6H_2(OMe) \cdot C(NOH) \cdot CMe{:}NOH$, which separates from aqueous alcohol in white crystals melting at 136°.

The *mercuric acetate* compound of *myristicin*,

$$CH_2{:}O_2{:}C_6H_2(OMe) \cdot C_3H_5(OH) \cdot Hg \cdot OAc,$$

prepared, together with a non-crystalline *isomeride*, by treating a benzene solution of myristicin (1 mol.) with a saturated aqueous solution of mercuric acetate (1 mol.), crystallises from benzene in white, mammillary masses melting at 111°. Treatment of an aqueous solution of this compound (1 mol.) with saturated potassium chloride (1 mol.) solution yields the *compound* $C_{11}H_{13}O_4ClHg$, separating from alcohol in white crystals melting at 127°.

*Dihydroxy*iso*myristicin*, $CH_2{:}O_2{:}C_6H_2(OMe) \cdot C_3H_5(OH)_2$, obtained by

the prolonged action of a saturated aqueous solution of mercuric acetate (4 mols.) on a benzene solution of *iso*myristicin (1 mol.), with subsequent reduction by means of zinc and potassium hydroxide solution, crystallises from ether in mammillary masses melting at 114—115°.

iso*Myristicin picrate*, $CH_2{:}O_2{:}C_6H_2(OMe){\cdot}C_3H_5,C_6H_3O_7N_3$, crystallises from alcohol in red needles melting at 86°. The ready formation of such a compound is characteristic of all propenyl compounds, especially those containing a methylenedioxy-group (compare Bruni and Tornani, Abstr., 1904, i, 875). T. H. P.

Condensation of Nitromalonaldehyde with Benzyl Methyl Ketone. Henry B. Hill and William J. Hale (*Amer. Chem. J.*, 1905, **33**, 1—21).—When benzyl methyl ketone reacts with the sodium derivative of nitromalonaldehyde, 5-nitro-2-hydroxydiphenyl is produced, which melts at 125—126° (corr.) (compare Borsche, Abstr., 1900, i, 594); its *sodium* derivative crystallises with $3\frac{1}{2}H_2O$. The *methyl ether* of 5-nitro-2-hydroxydiphenyl crystallises in colourless needles and melts at 95·2° (corr.); the *ethyl ether* melts at 110·6° (corr.), and the *benzoyl* derivative forms small, white, irregular prisms and melts at 99·3° (corr).

5-Amino-2-hydroxydiphenyl melts at 199° (corr.), diphenylquinone melts at 112—113° (corr.), and 3 : 5-dinitro-2-hydroxydiphenyl melts at 207—208° (corr.) (compare Borsche, Abstr., 1900, i, 24).

The *sodium* derivative of 3 : 5-dinitro-2-hydroxydiphenyl crystallises with $2H_2O$; the *methyl ether* crystallises in colourless leaflets and melts at 114—115° (corr.). When 3 : 5-dinitro-2-hydroxydiphenyl is reduced with tin and hydrochloric acid, the *hydrochloride* of 3 : 5-diamino-2-hydroxydiphenyl is produced, which forms colourless crystals; on treating this compound with potassium carbonate, a yellow, flocculent precipitate of the *base* is obtained, which becomes reddish-brown when dry, and is soluble in alcohol or glacial acetic acid.

On oxidising the methyl ether of 5-nitro-2-hydroxydiphenyl with a solution of chromium trioxide in glacial acetic acid, the methyl ether of 5-nitrosalicylic acid is produced, together with benzoic acid. The methyl ether of 3 : 5-dinitro-2-hydroxydiphenyl is oxidised by chromic acid with considerable difficulty, small quantities of the methyl ether of 3 : 5-dinitrosalicylic acid being produced.

When either 5-nitro-2-hydroxydiphenyl or 3 : 5-dinitro-2-hydroxydiphenyl is boiled with nitric acid of sp. gr. 1·40, carbon dioxide is evolved and *p*-nitrobenzoic acid is produced.

By the action of nitric acid of sp. gr. 1·40 on the methyl ether of 3 : 5-dinitro-2-hydroxydiphenyl, the *methyl ether* of 3 : 5 : 4′-trinitro-2-hydroxydiphenyl, $NO_2{\cdot}C_6H_4{\cdot}C_6H_2(NO_2)_2{\cdot}OMe$, is produced, which crystallises in prisms and melts at 170—171° (corr.). 3 : 5 : 4′-*Trinitro-2-hydroxydiphenyl*, obtained by hydrolysing the methyl ether with concentrated hydrochloric acid, crystallises in pale yellow prisms, melts at 163—164° (corr.), is readily soluble in benzene, ether, or chloroform, and fairly so in glacial acetic acid or carbon disulphide, and on oxidation with nitric acid yields *p*-nitrobenzoic acid; the *sodium* salt forms orange-red crystals.

When 5-nitro-2-hydroxydiphenyl methyl ether is boiled with a mixture of nitric and glacial acetic acids, the *methyl ether* of 5 : 4′-dinitro-2-hydroxydiphenyl, $NO_2\cdot C_6H_4\cdot C_6H_3(NO_2)\cdot OMe$, is produced, which crystallises in white, slender needles and melts at 222—223° (corr.); on hydrolysis with concentrated hydrochloric acid, it is converted into 5 : 4′-dinitro-2-hydroxydiphenyl, which crystallises in long, slender, pale yellow needles, melts at 224—225° (corr.), is readily soluble in alcohol, ether, chloroform, cr glacial acetic acid and moderately so in hot benzene, and on oxidation with nitric acid is converted into *p*-nitrobenzoic acid; the *sodium* salt crystallises in orange-red needles.

By the action of nitric acid of sp. gr. 1·40 on 5-nitro-2-hydroxydiphenyl methyl ether, the methyl ether of 3 : 5 : 4′-trinitro-2-hydroxydiphenyl is produced together with the *methyl ether* of the corresponding 5 : 2′ : 4′-trinitro-derivative, $C_6H_3(NO_2)_2\cdot C_6H_3(NO_2)\cdot OMe$; the latter compound crystallises in small flattened prisms and melts at 104—106° (corr.). 5 : 2′ : 4′-*Trinitro-2-hydroxydiphenyl*, obtained by hydrolysing the methyl ether with concentrated hydrochloric acid, crystallises in small, pointed, yellow prisms, melts at 152—153° (corr.), is readily soluble in chloroform and fairly so in glacial acetic acid, warm alcohol, or warm benzene, and on oxidation with nitric acid of sp. gr. 1·40 is converted into 2 : 4-dinitrobenzoic acid; the *sodium* derivative crystallises in orange-red needles. E. G.

A Correction [α-Nitrosoresorcinol Monoethyl Ethers]. FERDINAND HENRICH (*J. pr. Chem.*, 1905, [ii], **71**, 56. Compare Abstr., 1904, i, 1006).—The author misunderstood Wegscheider's views as to the nature of the two modifications of α-nitrosoresorcinol monoethyl ether (*Verh. deut. Naturf. Ärzte in Kassel*) and now finds them to agree with his own (*loc. cit.*). G. Y.

Oxidation Products of Octohydroanthracene. MARCEL GODCHOT (*Compt. rend.*, 1905, **140**, 250—252).—Octohydroanthracene (Abstr., 1904, i, 987) is readily oxidised by chromic acid to anthraquinone, but when the oxidation is effected in acetic acid solution at the ordinary temperature *dihydro-oxanthranol* and *hexahydroanthrone* are obtained. *Dihydro-oxanthranol*, $C_6H_4{<}\begin{matrix}C(OH)\\C(OH)\end{matrix}{>}C_6H_6$, crystallises from alcohol in large, yellow, prismatic needles melting at 159°, dissolves readily in hot alcohol, benzene, toluene, or acetic acid, is not fluorescent, and its solutions give a deep red coloration with alkalis. *Diacetyldihydro-oxanthranol*, $C_6H_4{<}\begin{matrix}C(OAc)\\C(OAc)\end{matrix}{>}C_6H_6$, crystallises in large, colourless needles melting at 220°, and soluble in hot alcohol, benzene, or acetic acid, the solutions in alcohol or acetic acid exhibiting a beautiful blue fluorescence. *Hexahydroanthrone*, $C_{14}H_{16}O$, crystallises in hard, clear plates, melts at 45·5°, boils at 222—225° under 25 mm. pressure, is readily soluble in all the ordinary organic solvents, slightly volatile with steam, and reduces Fehling's solution or ammoniacal silver nitrate. The *semicarbazone* crystallises in small, yellow, leafy crystals melting at 250°. Dibromohexahydroanthrone, $C_{14}H_{14}OBr_2$, forms prismatic crystals melting at 123—124°, readily soluble in alcohol, carbon bisulphide, or ether. M. A. W.

p-Dimethylaminobenzaldehyde. III. Action of Magnesium Organic Compounds. FRANZ SACHS and LUDWIG SACHS (*Ber.*, 1905, 38, 511—517. Compare Abstr., 1903, i, 37; 1904, i, 506).—p-*Dimethylaminophenylmethylcarbinol*, $NMe_2\cdot C_6H_4\cdot CHMe\cdot OH$, formed by the action of 1 mol. of p-dimethylaminobenzaldehyde on 1 mol. of magnesium and two mols. of methyl iodide in ethereal solution, crystallises in lemon-coloured, microscopic, prismatic, pointed leaflets, melts at 60·25°, is easily soluble in water and the usual organic solvents, and dissolves in concentrated sulphuric acid to a yellow solution, and in glacial acetic acid to a yellow solution which becomes green when heated; the *hydrochloride* is obtained as a white, flocculent, hygroscopic precipitate; the *platinichloride* forms a brownish-yellow, flocculent mass. Attempts to prepare the corresponding styrene by distillation of the carbinol, or by conversion into the chloride and heating with pyridine, or by treatment with either excess of magnesium methyl iodide or acetic anhydride were unsuccessful, chiefly owing to the formation of decomposition and polymerisation products.

p-*Dimethylaminophenylethylcarbinol*, $NMe_2\cdot C_6H_4\cdot CHEt\cdot OH$, formed by the action of p-dimethylaminobenzaldehyde on magnesium ethyl bromide in well-cooled ethereal solution, crystallises in needles, melts at 46°, gradually decomposes at the ordinary temperature, and is only slightly soluble in water, but easily so in the ordinary organic solvents; the *platinichloride* forms a yellow oil. When heated under 10 mm. pressure, the carbinol yields 4-dimethylamino-1-Δ^{α}-propenylbenzene (p-dimethylaminophenylpropylene), which distils at 152—154°, crystallises in microscopic, white needles, slowly decomposes at the ordinary temperature, and dissolves in concentrated sulphuric acid to a golden, in hot glacial acetic acid to a bluish-green, solution; the *platinichloride* crystallises in broad, yellow needles and melts at 132°.

p-*Dimethylaminophenylbenzylcarbinol*, $NMe_2\cdot C_6H_4\cdot CH(OH)\cdot CH_2Ph$, prepared by the action of the aldehyde on magnesium and benzyl chloride, crystallises in sheaves of white needles, melts at 59—60°, has a bitter flavour, and forms an oily *platinichloride*. p-*Dimethylaminostilbene*, $NMe_2\cdot C_6H_4\cdot CH:CHPh$, is formed on prolonged boiling of the carbinol in alcohol, or on heating the carbinol under 10 mm. pressure, when the stilbene distils at 251—252°. It crystallises in broad, glistening leaflets and melts at 147—148°. The *hydrochloride* crystallises in small, white leaflets and melts and decomposes at 174—175°; the *platinichloride* crystallises in small, colourless needles, rapidly becomes rust-coloured, and melts and decomposes at 168°; the *picrate* crystallises in brown, microscopic needles and melts at 158°; the *methiodide* crystallises in yellow leaflets and melts at 204° (corr.).

p-*Dimethylaminophenyl-α-naphthylcarbinol*,

$$NMe_2\cdot C_6H_4\cdot CH(OH)\cdot C_{10}H_7,$$

prepared by the action of the aldehyde on magnesium and α-bromonaphthalene, crystallises in white prisms, melts at 97—98°, and dissolves in mineral acids to form coloured solutions. The *platinichloride* crystallises in hexagonal leaflets which remain unchanged at 230°.

s-Diphenylcarbamide was the only product obtained by the action of phenylcarbimide on the above carbinols. G. Y.

Action of Magnesium Ethyl Iodide on Piperonaldehyde. New Synthesis of *iso*Safrole. EFISIO MAMELI (*Gazzetta*, 1904, **34**, ii, 409—419).—Besides the work already noticed (Abstr., 1904, i, 1023), a description is given of the *benzoyl* derivative of *ethylpiperonylcarbinol*, $CH_2{:}O_2{:}C_6H_3{\cdot}CHEt{\cdot}OBz$, which separates from benzene in white crystals melting at 112°. T. H. P.

Ethylpiperonyl Ether. EFISIO MAMELI (*Atti R. Accad. Lincei*, 1904, [v], **13**, ii, 611—614. Compare Abstr., 1904, i, 743).—When kept in an impure state, ethylpiperonylcarbinol (Abstr., 1904, i, 1023) becomes slowly etherified, yielding *ethylpiperonyl ether*,

$$\left(CH_2{<}\begin{array}{l}O{\cdot}C{\cdot}CH{:}CH\\ O{\cdot}C{\cdot}CH{:}C{\cdot}CHEt\end{array}\right)_2O,$$

which crystallises from benzene or alcohol in small, white prisms melting at 88°, dissolves readily in ether, light petroleum, chloroform, or pyridine, and slightly in acetic acid, and exhibits normal cryoscopic behaviour in benzene solution. It does not reduce ammoniacal silver nitrate or Fehling's solution, and does not combine with benzoyl chloride or phenylhydrazine. On treatment with concentrated sulphuric acid, the crystals become dark red, whilst the liquid assumes an intense blood-red coloration which changes to violet in a few hours. Concentrated nitric acid dissolves the ether with great energy, nitrous fumes being abundantly evolved; on adding water to the mixture, a nitro-derivative is precipitated. When heated, even under reduced pressure, the ether decomposes into water and *iso*safrole; this decomposition takes place in two stages, like that of the corresponding methyl compound (*loc. cit.*). T. H. P.

Reactions of Sodium Benzhydrol. RAYMOND FOSS BACON (*Amer. Chem. J.*, 1905, **33**, 68—97).—The *sodium* derivative of benzhydrol crystallises in large, transparent, colourless plates, turns green or greenish-blue on exposure to light, but becomes colourless again in the dark; it decomposes at 250° with formation of benzene, sodium benzoate, diphenylmethane, and sometimes tetraphenylethane and tetraphenylethylene. When dry air and oxygen are passed over sodium benzhydrol at the ordinary temperature, benzophenone, sodium peroxide, sodium carbonate, and a small quantity of sodium benzoate are produced. The reaction is considered to take place between the dissociated benzhydrol molecules and the active oxygen molecules in accordance with the following scheme: $CPh_2{:} + 2NaOH + O_2 \longrightarrow CPh_2(ONa)_2 + H_2O_2 \longrightarrow COPh_2 + Na_2O_2 + H_2O$. The amount of sodium peroxide present at the end of one experiment was found to be only 21·67 per cent. of the amount demanded by the equation, this being due to its reduction by the unchanged diphenylmethylene,

$$CPh_2{:} + Na_2O_2 \longrightarrow COPh_2 + Na_2O.$$

When bromodiphenylmethane is oxidised with potassium permanganate in presence of sulphuric acid, benzophenone is obtained. If dry oxygen is passed through bromodiphenylmethane at 160—170°,

hydrogen bromide is evolved and benzophenone is produced together with a small quantity of tetraphenylethylene. By the action of sodium on an ethereal solution of bromodiphenylmethane, tetraphenylethane and diphenylmethane are formed.

Conrad and Hodgkinson (Abstr., 1877, 590) have shown that when sodium reacts with benzyl acetate at 135°, benzyl acetoacetate is not produced, but the chief product is benzyl β-phenylpropionate. It is now found that benzyl ether is also formed in this reaction. The action of sodium on benzyl acetate and benzhydryl acetate in cold ethereal solution has been studied by Shaklee, who has found that the main products of the reaction are acetic acid and benzyl alcohol or benzhydrol respectively, a small amount of diacetyl being formed in each case.

Benzyl acetoacetate, which has been prepared by Shaklee by the action of benzyl alcohol on ethyl acetoacetate at 160°, is a colourless, mobile oil which boils at 162—164° under 16 mm. pressure, boils and decomposes at about 270° under the ordinary pressure, and gives a blood-red coloration with alcoholic ferric chloride; its *copper* derivative melts at 156°.

Benzhydryl acetoacetate, prepared in a similar manner, crystallises in colourless plates, melts at 56°, is very soluble in most organic solvents, and gives a deep purple coloration with ferric chloride; the *copper* derivative melts at 174—176°.

Experiments have shown that by the action of sodium or sodium benzyloxide on benzyl acetate at 100°, only traces of benzyl acetoacetate are produced, and that similarly only very small quantities of benzhydryl acetoacetate can be obtained by the action of sodium benzhydrol on benzhydryl acetate.

ββ-Diphenylpropionic acid melts at 155°, instead of 151° as stated by Henderson (Trans., 1891, **59**, 734). *Benzhydryl ββ-diphenylpropionate*, obtained by the action of bromodiphenylmethane on potassium ββ-diphenylpropionate at 150—160°, crystallises from alcohol in colourless needles, melts at 112°, and is readily soluble in benzene and sparingly so in ether.

When ethylacetanilide is heated for a considerable time with sodium benzhydrol in a sealed tube, ethylaniline, benzhydrol, benzhydryl ether, ββ-diphenylpropionic acid, and small quantities of benzophenone and tetraphenylethane are formed. If benzhydryl acetate is heated with quicklime in a sealed tube for 6 hours at 230—250°, ββ-diphenylpropionic acid, tetraphenylethane, benzhydryl ether, benzhydrol, and a small amount of benzophenone are produced.

By the interaction of benzhydryl acetate and sodium benzhydrol in a sealed tube at 150—160°, ββ-diphenylpropionic acid, benzhydryl ββ-diphenylpropionate, benzhydrol, benzhydryl ether, tetraphenylethylene, and small quantities of benzophenone and tetraphenylethane are formed. When benzhydryl acetate is heated with sodium at 130—140°, ββ-diphenylpropionic acid, benzhydrol, tetraphenylethylene, benzophenone, and traces of tetraphenylethane are produced. If sodium benzhydrol and benzhydryl acetate are heated together at 300—310° in a sealed tube, ββ-diphenylpropionic acid (75 per cent. of the theoretical yield), diphenylmethane, benzophenone, and a small quantity of benzoic acid are produced.

Benzhydryl formate, obtained by the action of potassium formate on bromodiphenylmethane, is a colourless oil which boils at 159—160° under 10 mm. pressure. When this ester is heated with sodium benzhydrol for 8 hours in a sealed tube at 300—310°, diphenylacetic acid is produced.

Benzhydryl iso*butyrate* is a crystalline substance which melts at 54°, boils at 185—187° under 15 mm. pressure, and is soluble in alcohol or ether. When this compound is heated with sodium benzhydrol in a sealed tube, ββ-diphenyl-αα-dimethylpropionic acid, benzhydrol, diphenylmethane, and benzophenone are produced. The results of several experiments show that the yield of ββ-diphenyl-αα-dimethylpropionic acid never exceeds 30 per cent., and that diphenylmethane and benzophenone are always obtained owing to the decomposition of a large proportion of the sodium benzhydrol.

Nef (Abstr., 1898, i, 106) has stated that benzhydryl acetate decomposes at 300° with formation of acetic acid, tetraphenylethylene, and tetraphenylethane. On repeating this experiment, acetic acid, tetraphenylethylene, benzophenone, and diphenylmethane were obtained, but tetraphenylethane was not produced.

Benzhydryl ethyl ether is decomposed at 300° into acetaldehyde, tetraphenylethane, and benzophenone.

Fromm and Achert (Abstr., 1903, i, 340) have shown that benzyl sulphide decomposes when heated with formation of hydrogen sulphide, toluene, stilbene, thionessal (tetraphenylthiophen), and *s*-tetraphenylbutane. These results can be explained on the supposition that the benzyl sulphide first undergoes dissociation into hydrogen sulphide (1 mol.) and phenylmethylene (2 mols.) This view is supported by the fact that when benzyl chloride is heated with anhydrous potassium oxalate, *s*-tetraphenylbutane is produced.

Benzyl β-phenylpropionate is a colourless oil which boils at 190—195° under 10 mm. pressure and is rapidly hydrolysed by alcoholic potassium hydroxide at the ordinary temperature.

The action of sodium on benzyl acetate has been studied by Conrad and Hodgkinson (*loc. cit.*). On repeating their experiments, it was found that the neutral and less volatile products obtained by them after treatment with alcoholic potassium hydroxide must have consisted largely of benzyl ether.

When a mixture of benzyl *iso*butyrate and sodium benzyloxide is heated at 300—310° in a sealed tube, benzyl alcohol, benzyl ether, *iso*butyric acid, benzoic acid, and traces of benzaldehyde are obtained, but α-benzyl*iso*butyric acid is not produced. It is probable that the substance described by Hodgkinson (Trans., 1878, **33**, 495) as benzyl α-benzyl*iso*butyrate consisted of benzyl ether. E. G.

Ketonic Decomposition of the Triphenylcarbinols. Otto Fischer and Walter Hess (*Ber.*, 1905, **38**, 335—339).—Trinitrotriphenylmethane is hardly affected by a boiling solution of chromic acid in acetic acid, but is decomposed when heated with nitric acid of sp. gr. 1·4 for 3 hours at 150°, giving 4 : 4′-dinitrobenzophenone ; small quantities of this substance are also formed in the preparation of

trinitrophenylcarbinol by the oxidation of trinitrotriphenylmethane by the air in presence of alkali.

Tri-p-*bromotriphenylmethane*, $C_{19}H_{13}Br_3$, prepared from *p*-leucaniline by means of the diazo-reaction, crystallises from light petroleum in thick, colourless prisms and melts at 112°; it is oxidised by chromic acid in acetic acid solution to a mixture of 20 per cent. of 4 : 4′-dibromobenzophenone and 80 per cent. of *tri*-p-*bromotriphenylcarbinol*, which crystallises from benzene or light petroleum in thick plates and melts at 133°.

Tri-p-*chlorotriphenylmethane* crystallises from light petroleum in prisms, melts at 87—88°, and on oxidation with chromic acid, as in the foregoing case, gives mostly *trichlorotriphenylcarbinol*, which separates from light petroleum containing benzene in thick crystals melting at 98°; a little dichlorobenzophenone is formed.

Tri-p-*iodotriphenylmethane* forms slightly yellow crystals, melts at 131—132°, and on oxidation with chromic acid gives principally *tri*-p-*iodotriphenylcarbinol*, although some 4 : 4′-di-iodobenzophenone is formed; the carbinol crystallises in long, yellow prisms and melts at 155°. W. A. D.

ε-Halogen Derivatives of Amylamine. JULIUS VON BRAUN and A. STEINDORFF (*Ber.*, 1905, **38**, 169—179).—*Benzoyl-ε-phenoxyamylamide*, $NHBz\cdot[CH_2]_5\cdot OPh$, prepared by warming an alcoholic solution of benzoyl-ε-chloroamylamide with phenol and sodium, separates from a mixture of ethyl alcohol and water in glistening leaflets and melts at 89°. When heated with three times its amount of hydrobromic acid, saturated at 0°, for 4 hours at 150° in a sealed tube, it formed ε-bromoamylamine hydrobromide, which was converted into the free base, $C_5H_{10}Br\cdot NH_2$, the *platinichloride* of which was analysed.

Benzoyl-ε-bromoamylamide, $NHBz\cdot C_5H_{10}Br$, forms snow-white crystals and melts at 59—61°.

When an alcoholic solution of benzoyl-ε-chloroamylamide is boiled with sodium iodide, *benzoyl-ε-iodoamylamide*, $NHBz\cdot C_5H_{10}I$, is formed; it crystallises in prisms and melts at 54—55°. *ε-Iodoamylamine*, prepared by heating its benzoyl derivative with fuming hydriodic acid in a sealed tube at 150° and then adding alkali, readily undergoes transformation when heated into piperidine hydriodide, thus:

$$NH_2\cdot C_5H_{10}I = C_5NH_{11},HI.$$

Benzoyl-ε-iodoamylamide is more reactive than the corresponding bromo-compound. Whilst the latter reacts with difficulty with secondary bases, the former reacts with great readiness even at the ordinary temperature.

Benzoylpiperidylcadaverine, $NHBz\cdot[CH_2]_5\cdot C_5NH_{10}$, formed by the action of benzoyl-ε-iodoamylamide on piperidine, separates from light petroleum in glistening crystals and melts at 74°. It dissolves readily in dilute acids; its *picrate* melts at 104°.

ε-Benzoylamino-n-*hexonitrile* (*benzoyl-ε-leucine nitrile*),

$$NHBz\cdot[CH_2]_5\cdot CN,$$

prepared by the action of benzoyl-ε-iodoamylamide on a solution of potassium cyanide in a mixture of water and alcohol, separates from

water or dilute alcohol in snow-white, glistening leaflets and melts at 95°. When hydrolysed, it forms ε-leucine, $NH_2\cdot[CH_2]_5\cdot CO_2H$, whilst by reduction and subsequent hydrolysis, hexamethylenediamine, $NH_2\cdot[CH_2]_6\cdot NH_2$, is produced.

By the action of phosphorus pentachloride on benzoylamino-ε-hexonitrile, the imide chloride, $CPhCl:N\cdot[CH_2]_5\cdot CN$, is formed, which, on elevation of temperature, is transformed into a mixture of benzonitrile and ε-chlorohexonitrile, $C_5H_{10}Cl\cdot CN$. When the latter compound is mixed with a solution of phenol and sodium in ethyl alcohol, *ε-phenoxyhexonitrile*, $OPh\cdot[CH_2]_5\cdot CN$, is formed as snow-white crystals which melt at 36°. A. McK.

Reaction between Organic Magnesium Compounds and Unsaturated Compounds. II. Reactions with Derivatives of Cinnamic Acid. Elmer P. Kohler and Gertrude Heritage (*Amer. Chem. J.*, 1905, **33**, 21—35. Compare Abstr., 1904, i, 595).—When an ethereal solution of methyl cinnamate is added gradually to a solution of magnesium phenyl bromide at −10° and the resulting yellow magnesium compound is decomposed by shaking with finely-crushed ice, on dissolving the magnesium salts in hydrochloric acid at 0°, diphenylpropiophenone is produced together with *methyl ββ-diphenylpropionate*, which crystallises in large, lustrous prisms and melts at 47°; a number of other substances are simultaneously formed. By the action of benzoyl chloride on the magnesium compound, benzoyltriphenylpropenol is obtained together with a *benzoate*, $C_{23}H_{20}O_3$, which crystallises in long, white, silky needles, melts at 130—133°, and is easily hydrolysed with formation of benzoic acid and methyl diphenylpropionate. The relative amounts of diphenylpropiophenone and methyl ββ-diphenylpropionate produced vary with the temperature. At −10°, the quantity of the ketone obtained rarely exceeds 5 per cent. of the total product, whilst at 35° as much as 20 per cent. is formed. In the case of ethyl cinnamate, only a trace of ketone is produced at −10°, and less than 10 per cent. at 35°. The amyl ester yields only a trace of ketone at 35° and none at −10°.

By the action of magnesium methyl iodide on methyl cinnamate, dimethylstyrylcarbinol, $CHPh:CH\cdot CMe_2\cdot OH$, is produced, which, on oxidation with potassium permanganate, is converted into benzoic and hydroxy*iso*butyric acids. An oily *substance*, $C_{22}H_{26}O$, probably the ether, $O(CMe_2\cdot CH:CHPh)_2$, amounting to less than 5 per cent. of the total product, is also formed, which boils at 128° under 11 mm. pressure, combines with bromine, and is oxidised by hot alkaline potassium permanganate; under certain conditions, benzylideneacetone is also produced.

By the action of magnesium phenyl bromide on cinnamyl chloride, diphenylpropiophenone, cinnamic acid, and ββ-diphenylpropionic acid are obtained, together with other compounds.

Cinnamylethylanilide, $CHPh:CH\cdot CO\cdot NPhEt$, obtained by the action of cinnamyl chloride on ethylaniline, crystallises in large, colourless prisms, melts at 74°, and is readily soluble in ether, alcohol, chloroform, or carbon disulphide and moderately so in boiling light petroleum. When this substance is treated with magnesium phenyl

bromide, ββ-diphenylpropionylethylanilide is produced, which is converted by bromine into *diphenylbromopropionylethylanilide*. This compound crystallises in large, colourless prisms, melts at 178°, is readily soluble in chloroform, acetone, or boiling alcohol, and is hydrolysed by hydrochloric acid with formation of *α-bromo-ββ-diphenylpropionic acid*, $CHPh_2 \cdot CHBr \cdot CO_2H$, which melts and decomposes at about 164°, is readily soluble in alcohol or ether, and when boiled with alcoholic potassium hydroxide is converted into β-phenylcinnamic acid. An attempt was made to prepare α-bromo-ββ-diphenylpropionic acid by the direct bromination of diphenylcinnamic acid, but it was found that the main product of the reaction was phenylhydrindone.

β-Phenylcinnamic acid, $CPh_2 \colon CH \cdot CO_2H$, crystallises in colourless needles, melts at 142°, is readily soluble in alcohol or ether, and moderately so in boiling water, does not combine with bromine at the ordinary temperature, but is oxidised by cold potassium permanganate solution with formation of benzophenone and carbon dioxide.

E. G.

Reaction between Unsaturated Compounds and Organic Magnesium Compounds. IV. Reactions with Esters of α-Phenylcinnamic Acid. Elmer P. Kohler and Gertrude Heritage (*Amer. Chem. J.*, 1905, **33**, 153—163).—When an ethereal solution of methyl α-phenylcinnamate is treated with magnesium phenyl bromide, the *compound* $CHPh_2 \cdot CPh \colon C(OMgBr) \cdot OMe$, is produced, which crystallises in small, lustrous prisms and if left for a day changes into a thick paste. By extracting this paste with chloroform, *methyl αββ-triphenylpropionate*, $CHPh_2 \cdot CHPh \cdot CO_2Me$, is obtained, which crystallises in hard, lustrous plates and melts at 159°. *αββ-Triphenylpropionic acid* crystallises in needles, melts at 211°, and is readily soluble in alcohol or ether, sparingly so in light petroleum, and insoluble in water. The *ethyl* ester crystallises in plates and melts at 120°.

When the additive compound of methyl α-phenylcinnamate with magnesium phenyl bromide is treated with dry hydrogen chloride, methyl triphenylpropionate and magnesium chloride are produced. It reacts with acetyl chloride with formation of the *compound* $CHPh_2 \cdot CPh \colon C(OAc) \cdot OMe$, which crystallises from alcohol in plates, melts at 75°, and on hydrolysis yields acetic acid and methyl triphenylpropionate. By the action of bromine on the magnesium compound, *methyl triphenylbromopropionate*, $CHPh_2 \cdot CPhBr \cdot CO_2Me$, is produced, which crystallises in large, colourless prisms, melts and decomposes at 150—152°, and is readily soluble in chloroform or hot acetone and slightly so in alcohol or ether. When this ester is boiled with alcoholic potassium hydroxide, it is converted into triphenylacrylic acid, melting at 213°.

When methyl α-phenylcinnamate is treated with magnesium *o*-tolyl bromide, an additive *compound* separates in colourless crystals which, on decomposition with water, yields *methyl* o-*tolyldiphenylpropionate*, $C_7H_7 \cdot CHPh \cdot CHPh \cdot CO_2Me$. This ester crystallises in hard, lustrous plates, melts at 150°, and on hydrolysis is converted into o-*tolyldi-*

phenylpropionic acid, which crystallises in long needles and melts at 190°.

By the action of magnesium α-naphthyl bromide on methyl α-phenylcinnamate, an additive compound is produced which, on decomposition, yields *methyl β-1-naphthyl-αβ-diphenylpropionate*,

$$C_{10}H_7\cdot CHPh\cdot CHPh\cdot CO_2Me,$$

which crystallises in small, lustrous pyramids or prisms, melts at 170°, and is readily soluble in chloroform, ether, or light petroleum. Another *methyl* ester is simultaneously produced which crystallises in large, lustrous prisms, melts at 128°, and is more soluble in organic solvents than the isomeride melting at 170°. These esters are perhaps stereoisomeric, but as they furnish the same acid on hydrolysis it is not possible to prove that they represent two racemic modifications. *β-1-Naphthyl-αβ-diphenylpropionic acid* crystallises in short, thick needles and melts at 171°.

When methyl α-phenylcinnamate is treated with magnesium methyl iodide, *γδ-diphenyl-β-methyl-Δ^γ-buten-β-ol*, $CHPh\colon CPh\cdot CMe_2\cdot OH$, is produced, which crystallises in thin plates or long, flat needles, melts at 68°, is readily soluble in acetone or ether and fairly so in light petroleum, is oxidised by alkaline permanganate with formation of benzoic and acetic acids, and does not combine with bromine.

E. G.

Mechanism of the Synthesis of Salicylic Acid. Cornelis A. Lobry de Bruyn and S. Tijmstra (*Rec. trav. chim.*, 1904, **23**, 385—393).—When sodium phenyl carbonate is heated, its tension of dissociation becomes equal to the atmosphere at 85°; beyond this, it increases until the temperature reaches 100° and then diminishes, this being due to the reabsorption of carbon dioxide and the formation of salicylic acid. These observations indicate that sodium phenyl carbonate may be an intermediate product in the production of sodium salicylate by Schmitt's method (Abstr., 1885, 709 and 982), but that it does not play this *rôle* under the conditions prescribed by Kolbe. It is suggested that in Kolbe's process the sodium phenoxide is first converted into the corresponding *o*-carboxylic acid, $ONa\cdot C_6H_4\cdot CO_2H$, and that this then undergoes isomeric transformation into sodium salicylate.

Sodium phenoxide o-*carboxylic acid* (o-*sodoxybenzoic acid*) may be obtained as a white, crystalline powder by heating sodium phenyl carbonate in closed tubes at 100° for four days. When mixed with sodium phenoxide and heated at 150° in closed tubes, it furnishes disodium salicylate and phenol, and when heated with methyl iodide it yields methyl salicylate, probably as the result of isomeric transformation of the anisole-*o*-carboxylic acid first formed, since the latter, when heated during one day at 150° in the presence of small quantities of *o*-sodoxybenzoic acid, is completely converted into methyl salicylate. It is probable that there is also no intermediate formation of carbonates in the preparation of carboxylic acids from phloroglucinol (Will, Abstr., 1885, 906) or resorcinol (Senhofer and Brunner, Abstr., 1881, 265), but this may occur with hydroxyquinoline (Schmitt and Engelmann, Abstr., 1887, 738; 1888, 66).

T. A. H.

Action of Organo-magnesium Compounds on Phthalic Anhydride. HUGO BAUER (*Ber.*, 1905, **38**, 240—241. Compare Abstr., 1904, 417).—*Phthalophenone*, $C_6H_4<{CPh_2 \atop CO}>O$, melting at 115°, is formed by the interaction of magnesium phenyl bromide and phthalic anhydride along with small quantities of a compound melting at 146°, probably identical with Zincke's β-dibenzoylbenzene. Further, the crude reaction mixture, on the addition of dilute sulphuric acid, yields a viscid, yellow oil soluble in light petroleum with a green fluorescence; in time, the fluorescence disappears and phthalophenone crystallises out. *Dibenzylphthalide*, $C_6H_4<{C(C_7H_7)_2 \atop CO}>O$, forms colourless needles melting at 203—204°. By the interaction of magnesium *p*-tolyl bromide and phthalic anhydride, a brown resin is formed from which a compound, possibly *o-ditoluoylbenzene*, melting at 189—190°, isomeric with ditolylphthalide, was isolated. E. F. A.

Ethylidenephthalide. ADOLF DAUBE (*Ber.*, 1905, **38**, 206—209). —The ethylidenephthalide was prepared by Gottlieb's method (Abstr., 1899, i, 511) and hydrolysed to propiophenone-*o*-carboxylic acid.

This acid readily reacts with hydroxylamine yielding the *anhydride of propiophenoneoxime-o-carboxylic acid*, $C_6H_4<{CEt:N \atop CO-O}$, which crystallises from hot water in prisms melting at 119°.

Hydrazine converts the acid into 1-ethylphthalazone (Paul, Abstr., 1899, i, 776), which can be readily alkylated, yielding 1 : 3-*diethylphthalazone*, $C_6H_4<{CEt:N \atop CO-NEt}$. This melts at 49—50° and distils at 307°. Phosphorus oxychloride reacts with ethylphthalazone, yielding 4-*chloro*-1-*ethylphthalazine*, $C_6H_4<{CEt:N \atop CCl:N}$, which crystallises from alcohol in needles melting at 93°. On reduction with tin and hydrochloric acid, it yields *ethyldihydroisoindole*, $C_6H_4<{CHEt \atop CH_2}>NH$, which boils at 327—329°.

The chloro-compound readily reacts with sodium alkyloxides. 4-*Methoxy*-1-*ethylphthalazine* melts at 49°, the *ethoxy*-compound at 53°, and the *phenoxy*-derivative at 89°.

Ethylphthalimidine, $C_6H_4<{CHEt \atop CO}>NH$, obtained by the reduction of ethylphthalazone with zinc and hydrochloric acid, forms colourless crystals melting at 105° and turning red on exposure to the air.

Ethylidenephthalide yields an additive product with nitric peroxide; when this is crystallised from glacial acetic acid, a small amount of *nitroethylidenephthalide*, $NO_2\cdot CMe:C<{O \atop C_6H_4}>CO$, is obtained. It crystallises in yellow needles melting at 123°. J. J. S.

Tolylnaphthalimides and Naphthylnaphthalimides. GUIDO BARGELLINI (*Gazzetta*, 1904, **34**, ii, 454—459).—The author has prepared *o*-tolylnaphthalimide by the interaction of naphthalic anhydride

and *o*-toluidine, and finds that it crystallises from acetic acid in yellow needles melting at 217—218°; Jaubert (Abstr., 1895, i, 239) gave 214°.

m-*Tolylnaphthalimide*, $C_{10}H_6{<}{}^{CO}_{CO}{>}N{\cdot}C_6H_4Me$, crystallises from alcohol in shining, yellow needles melting at 175—176° and dissolves readily in acetic acid, ethyl acetate, or chloroform and to a slight extent in ether, benzene, or carbon disulphide.

p-*Tolylnaphthalimide*, $C_{19}H_{13}O_2N$, crystallises from acetic acid in small, yellow needles melting at 304—305° and dissolves readily in chloroform and slightly in alcohol, carbon disulphide, benzene, or ethyl acetate.

a-Naphthylnaphthalimide, $C_{10}H_6{<}{}^{CO}_{CO}{>}N{\cdot}C_{10}H_7$, separates from acetic acid as a yellow, crystalline powder melting at 214—215°, and is very soluble in carbon disulphide, chloroform, or nitrobenzene, and slightly so in ether, light petroleum, ethyl acetate, acetone, benzene, or methyl, ethyl, or amyl alcohol.

β-Naphthylnaphthalimide, $C_{22}H_{13}O_2N$, crystallises from acetic acid in yellow needles melting at 291—292° and dissolves readily in chloroform or nitrobenzene, less so in methyl, ethyl, or amyl alcohol, benzene, ethyl acetate or acetone, and to a slight extent in ether, carbon disulphide, or light petroleum. T. H. P.

The Oxonium Nature of Santonin. EDGAR WEDEKIND and A. KOCH (*Ber.*, 1905, **38**, 421—428).—Santonin and such of its derivatives as contain the carbonyl group intact behave as oxonium compounds, and yield salts with acids and double compounds with certain metallic haloids. Desmotroposantonin and other enolic derivatives have no basic properties.

Santonin nitrate, $C_{15}H_{18}O_3,HNO_3$, forms colourless crystals and decomposes at 145°; it is stable in dry air, but is decomposed quantitatively into its components by water (compare Andreocci, *Atti R. Accad. Lincei*, 1896, [v], **5**, ii, 309).

Santonin antimony pentachloride, $2C_{15}H_{18}O_3,SbCl_5,HCl$, prepared by mixing the components slowly in glacial acetic acid solution, forms colourless needles and decomposes at 145°. It dissolves readily in most organic solvents; water and alcohols decompose it. The rotation in acetone solution is that due to the santonin present. The hydrogen chloride in the salt is produced by chlorination of a part of the santonin (compare following abstract). *Santonic acid antimony pentachloride* forms stable crystals and decomposes at 145°.

Santonin tin tetrabromide, $2C_{15}H_{18}O_3,SnBr_4,HBr$, forms yellow prisms and decomposes at 127°.

Oxonium salts of similarly abnormal composition have been described by Rosenheim and Levy (Abstr., 1904, i, 1024).

Santonin ferric chloride forms brown crystals and melts and decomposes at 210°; the bright yellow *platinichloride* is unstable. It was not found possible to prepare a hydrochloride, oxalate, or picrate; the ferro-, ferri-, and cobalti-cyanides will be described shortly.

C. H. D.

The Behaviour of Halogens towards Santonin. EDGAR WEDEKIND and A. KOCH (*Ber.*, 1905, **38**, 429—435. Compare preceding abstract).—It was not found possible to prepare bromo-substituted derivatives of santonin as described by Klein (Abstr., 1893, i, 112). Santonin reacts with bromine in acetic acid or chloroform solution to form a complex *oxonium bromide*, $C_{30}H_{37}O_6Br_3$, which contains two atoms of active bromine and one atom as hydrogen bromide, and thus has the constitution

$$C_{13}H_{16}O_2<\begin{matrix}CH_2\\ \vert\\ CO\!:\!HBr\end{matrix},C_{13}H_{16}O_2<\begin{matrix}CH_2\\ \vert\\ CO\!:\!Br_2\end{matrix}.$$

It decomposes at 105° and slowly loses bromine under the action of light.

Santonin oxonium iodide, $C_{30}H_{37}O_6I_3$, forms dark olive-green tablets with metallic reflex, stable in dry air, and decomposes at 135°. It is less readily decomposed by water than the bromide.

The behaviour of chlorine is quite different from that of bromine, only substitution derivatives being formed. Dichlorosantonin,

$$C_{15}H_{16}O_3Cl_2,$$

prepared from santonin and dry chlorine in chloroform solution, forms long, colourless prisms, becomes yellow at 140° and decomposes at 175°. Chlorine water reacts with santonin, forming chlorosantonin, $C_{15}H_{17}O_3Cl$, which crystallises from dilute alcohol and melts and decomposes at 235°. C. H. D.

Compounds from Lichen. WILHELM ZOPF (*Annalen*, 1905, **338**, 35—70. Compare Abstr., 1904, i, 1020).—Hesse's formula, $C_{28}H_{22}O_7$, for rhizocarpic acid is incorrect, the molecular formula being $(C_{13}H_{10}O_3)_2$.

Pseudovernia ericetorum contains atranoric acid, physodalin (Hesse's physodic acid), and a bitter material, but no furfuracic acid, isidic acid, or olivetoric acid. The *physodalin* forms crystals melting at 201—202°, and yields a *diacetyl* derivative melting at 158°. Hesse's lepraric acid could not be found in *Lepraria chlorina*.

Lepraria flava contains calycin, pinastric acid, and calyciarin. The last mentioned crystallises in rhombic plates and is insoluble in alkali hydroxides. *Lecanora varia* yields psoromic acid and *l*-usnic acid, the latter having $[\alpha]_D$ $-489{\cdot}2°$ in chloroform at 17°. *Catocarpus oreïtes* contains rhizocarpic acid and psoromic acid. *Usnea Schraderi* contains usnaric acid, *d*-usnic acid ($[\alpha]_D$ $+498{\cdot}3°$ in chloroform), and a colourless substance which could not be identified. Hesse's ochrolechiaic acid, obtained from *Ochrolechia pallescens* var. *parella*, is identical with variolaric acid; the former melts at about 280°, the latter at 283°. *Parmelia revoluta* yields atranoric acid and gryophoric acid. The latter acid is characterised by a very delicate blood-red coloration with bleaching powder. *Parmelia pilosella* yields atranoric acid and a crystalline bitter material, *pilosellic acid*; the latter melts at 245° and gives a violet coloration with ferric chloride and a yellow solution with potassium hydroxide and ammonia. From *Stictina gilva*, stictinin was isolated, which crystallises in needles melting at 160—161°, giving a reddish-violet coloration with ferric chloride and a cinnabar-red coloration with concentrated sulphuric acid, changing to an

orange-yellow solution with more acid. Rhizocarpic acid was found in *Calycium hyperellum*. K. J. P. O.

o-Methylaminobenzaldehyde. OTTO SCHMIDT (*Ber.*, 1905, **38**, 200—203. Compare Heller, Abstr., 1904, i, 160; Bamberger, *ibid.*, 422).—The physical constants of Heller's methylanthranil indicate that it cannot be a homologue of anthranil, but rather a mixture of methyl- and dimethyl-o-aminobenzaldehydes. Refractrometric determinations have shown that the group N·C:C·CO always produces an abnormally high refraction in a compound.

	Sp. gr.	at t.	n_D.	M_D.
o-Methylaminobenzaldehyde...	1·1092	11·8°/4°	1·62773	43·177
Methyl methylanthranilate ...	1·1348	12·3 /4	1·58395	48·658
Ethyl aminoacetate	1·0358	11·8 /4	1·42737	25·55
Acetylanthranil	1·2034	73·3 /4	1·56862	43·81

(Compare Brühl, Abstr., 1904, i, 92 and 160.) J. J. S.

β-Hydroxynaphthaldehyde. MARIO BETTI and CURIO M. MUNDICI (*Atti R. Accad. Lincei*, 1904, [v], **13**, ii, 542—550).—β-Hydroxynaphthaldehydephenylhydrazone and β-hydroxynaphthylideneaniline have already been described (Gattermann and Horlacher, Abstr., 1899, i, 372).

β-Hydroxynaphthylidene-p-nitroaniline, $OH\cdot C_{10}H_6\cdot CH{:}N\cdot C_6H_4\cdot NO_2$, crystallises from alcohol in dark red needles showing a metallic green reflex, or from benzene in yellowish-red scales or ruby-red plates melting at 222°.

1:2-*Naphthacoumarincarboxylic acid*, $C_{10}H_6{<}\begin{matrix}CH{:}C\cdot CO_2H\\ O-CO\end{matrix}$, prepared by the condensation of β-hydroxynaphthaldehyde and malonic acid in presence of acetic acid, crystallises from alcohol in scales or in yellow, silky needles melting and decomposing at 233°; the alcoholic solution exhibits vivid yellowish-blue fluorescence, and is faintly alkaline to litmus.

The action of dry hydrogen chloride on β-hydroxynaphthaldehyde in methyl alcoholic solution yields a *hydrochloride* of *dinaphthaxanthydrole*, $CH{<}\begin{matrix}C_{10}H_6\\ C_{10}H_6\end{matrix}{>}O\cdot Cl$, separating as a green, crystalline mass, which dissolves in acetic acid giving an intensely brown coloration, and is decomposed by water even in the cold; at 115°, it forms drops, and at 216—218° it melts and decomposes. When treated with methyl alcohol in the cold, it yields the corresponding *methyl* derivative, $OMe\cdot CH{<}\begin{matrix}C_{10}H_6\\ C_{10}H_6\end{matrix}{>}O$, which crystallises from methyl alcohol in pale yellow, strongly refracting prisms melting at 178°. Cold ethyl alcohol yields (1) the *ethyl* derivative, $C_{23}H_{18}O_2$, which crystallises from alcohol in colourless, silky needles melting at 149° and reddening slightly in the air; it has the normal molecular weight in freezing benzene, and forms a bright red *picrate* melting at 241°; (2) dinaphthaxanthene, $CH_2{<}\begin{matrix}C_{10}H_6\\ C_{10}H_6\end{matrix}{>}O$, which is obtained in larger yield by

the action of hot ethyl alcohol on the hydrochloride, and crystallises from benzene in shining, colourless needles melting at 203—204°.

T. H. P.

The 3-Methyl-6-alkyl*cyclo*hexanones and the Corresponding Phenols, Homologues of Menthone and Menthol. ALBIN HALLER (*Compt. rend.*, 1905, **140**, 127—130).—When the sodium derivative of 3-methyl*cyclo*hexanone, prepared by the action of sodamide on the ketone, is treated with an alkyl iodide, the corresponding 3-methyl-6-alkyl*cyclo*hexanone is obtained (compare Abstr., 1904, i, 600). By the prolonged action of methyl iodide on the sodium derivative of 3-methyl*cyclo*hexanone a mixture of the *di-*, *tri-*, *tetra-*, and *penta-methyl*cyclo*hexanones* is formed. 3-*Methyl*-6-*ethyl*cyclo*hexanone*, $C_9H_{16}O$, boils at 83—84° under 18 mm. pressure, has a sp. gr. 0·9016 at 15°/4° and $[\alpha]_D+8°32'$, and yields a *semicarbazone* melting at 152—154°. 3-*Methyl*-6-*propyl*cyclo*hexanone*, $C_{10}H_{18}O$, boils at 97—98° under 18 mm. pressure, has a sp. gr. 0·8994 at 15°/4° and $[\alpha]_D+3°21'$; its *semicarbazone* melts at 154—156°. 3-*Methyl*-6-*allyl*cyclo*hexanone*, $C_{10}H_{16}O$, boils at 98—99° under 18 mm. pressure, has a sp. gr. 0·9233 at 15°/4°, and $[\alpha]_D+18°2'$; its *semicarbazone* melts at 146—148°. 3-*Methyldiallyl*cyclo*hexanone*, $C_{13}H_{20}O$, boils at 130—132° under 20 mm. pressure, has a sp. gr. 0·9365 at 15°/4°, and $[\alpha]_D+62°2'$; its *semicarbazone* melts at 141—143°. 3-*Methyl*-6-iso*butyl*cyclo*hexanone*, $C_{11}H_{20}O$, boils at 93—95° under 11 mm. pressure, has a sp. gr. 0·9950 at 15°/4° and $[\alpha]_D+0°24'$; its semicarbazone melts at 171—173°.

The 3-methyl-6-alkyl*cyclo*hexanones, on reduction with sodium in absolute alcohol, yield the corresponding phenols, which have an odour similar to that of menthol, boil at a slightly higher temperature than the ketone from which they are derived, and form condensation products with benzaldehyde which are oxidised by potassium permanganate to form the α-methyl-δ-alkyladipic acid and benzoic acid according to the equation $CH_2<\begin{matrix}CH_2\cdot CHMe\\CHR—CO\end{matrix}>C:CHPh + O =$ $CO_2H\cdot CHMe\cdot CH_2\cdot CH_2\cdot CHR\cdot CO_2H + PhCO_2H$.

3-*Methyl*-6-*ethyl*cyclo*hexanol*, $C_9H_{18}O$, boils at 85—87° under 11 mm. pressure; 3-*methyl*-6-*propyl*cyclo*hexanol*, $C_{10}H_{20}O$, distils at 102—104° under 15 mm. pressure. 3-*Methyl*-6-*allyl*cyclo*hexanol*, $C_{10}H_{18}O$, boils at 98—100° under 10 mm. pressure. 3-*Methyl*-6-iso*butyl*cyclo*hexanol*, $C_{11}H_{22}O$, crystallises from light petroleum in thin needles melting at 68—69°; a liquid stereoisomeride boils at 110—112° under 16 mm. pressure.

M. A. W.

Condensation of Imines with Aldehydes and Ketones. CHARLES MAYER (*Bull. Soc. chim.*, 1905, [iii], **33**, 157—162. Compare Abstr., 1904, i, 832).—When molecular solutions of acetophenone and benzylideneaniline in alcohol are mixed, anilinobenzylacetophenone, $COPh\cdot CH_2\cdot CHPh\cdot NHPh$, is formed (Tambor and Wildi, Abstr., 1898, i, 313); from this, by the action of sulphuric acid, benzylideneacetophenone is produced. With benzylidene *p*-toluidine, p-*toluidinobenzylacetophenone*, $COPh\cdot CH_2\cdot CHPh\cdot NH\cdot C_6H_4Me$, is obtained; this separates

from alcohol in small, colourless needles and melts at 172°. *β-Naphthylaminobenzylacetophenone*, $COPh\cdot CH_2\cdot CHPh\cdot NH\cdot C_{10}H_7$, obtained by the interaction of acetophenone and benzylidene-β-naphthylamine, dissolved in alcohol, in presence of sodium methoxide, crystallises from boiling benzene in small needles, melts at 199°, and is slightly soluble in cold alcohol, more so on warming.

β-Anilino-β-phenyldiethyl ketone, $NHPh\cdot CHPh\cdot CH_2\cdot COEt$, obtained by the interaction of methyl ethyl ketone with benzylideneaniline, crystallises from alcohol in small, colourless needles, melts at 121°, and is slightly soluble in cold alcohol, more so on warming. The solution in sulphuric acid furnishes on addition of excess of water benzylidenemethyl ethyl ketone, $CHPh\colon CH\cdot COEt$ (Harries and Müller, Abstr., 1902, i, 295), instead of the quinoline derivative expected (compare Simon and Conduché, Abstr., 1904, i, 521). *β-Anilino-β-phenylethyl propyl ketone*, $NHPh\cdot CHPh\cdot CH_2\cdot COPr^{\alpha}$, forms small needles and melts at 88°. *β-Anilino-β-phenylethyl hexyl ketone*,

$$NHPh\cdot CHPh\cdot CH_2\cdot CO\cdot C_6H_{13},$$

forms colourless needles, melts at 92—93°, and is converted by sulphuric acid into *benzylidenemethyl hexyl ketone*, $CHPh\colon CH\cdot CO\cdot C_6H_{13}$, which forms colourless needles melting at 34°. *β-Anilino-β-phenylethyl heptyl ketone*, $NHPh\cdot CHPh\cdot CH_2\cdot CO\cdot C_7H_{15}$, crystallises in needles, melts at 93—94°, is slightly soluble in alcohol, readily so in ether, and with sulphuric acid yields *benzylidenemethyl heptyl ketone*, which crystallises from light petroleum in needles and from methyl alcohol in scales, melts at 52°, and is soluble in ether. *β-Anilino-β-phenylethyl nonyl ketone* forms small needles, melts at 96°, and furnishes benzylidenemethyl nonyl ketone. T. A. H.

Reactions between Organic Magnesium Compounds and Unsaturated Compounds. III. Reactions with Compounds containing Bromine. Elmer P. Kohler and Ruth M. Johnstin (*Amer. Chem. J.*, 1905, **33**, 35—45. Compare Abstr., 1904, i, 595, and this vol., i, 207, 208).—When an ethereal solution of ethyl α-bromocinnamate is added gradually to a solution of magnesium phenyl bromide and the resulting yellow precipitate is decomposed with ice-water, bromodiphenylpropiophenone (Kohler, Abstr., 1904, i, 596) is produced, together with benzoic acid and β-phenylcinnamic acid.

By the action of magnesium methyl iodide on ethyl α-bromocinnamate, an oily product is obtained which does not contain an ester and is slowly decomposed by boiling alcoholic potassium hydroxide with formation of potassium bromide, potassium benzoate, and a gum. When the oil is oxidised with dilute potassium permanganate, acetone, benzoic acid, and probably hydroxy*iso*butyric acid are obtained, whence it is concluded that the chief product of the reaction is a tertiary alcohol, $CHPh\colon CBr\cdot CMe_2\cdot OH$.

When α-bromobenzylideneacetophenone is treated with magnesium phenyl bromide and the product decomposed with ice-water, a nearly theoretical yield of α-bromo-ββ-diphenylpropiophenone is produced. *Phenylbenzylideneacetophenone*, $CPh_2\colon CH\cdot COPh$, obtained by the action of boiling alcoholic potassium hydroxide on bromodiphenylpropiophenone, crystallises in large, lemon-yellow prisms, melts at 92°, is

readily soluble in alcohol or ether and slightly so in light petroleum, and on oxidation with dilute potassium permanganate is converted into benzophenone and benzoic acid.

By the action of magnesium phenyl bromide on stilbene bromide, diphenyl is produced. Magnesium phenyl bromide reacts with ethyl dibromophenylpropionate with formation of diphenylpropiophenone and ethyl diphenylpropionate.

When benzylideneacetophenone bromide is slowly added to a solution of magnesium phenyl bromide at a low temperature, bromodiphenylpropiophenone and diphenylpropiophenone are produced, but if the reaction is carried out at 35° the products consist of diphenyl and diphenylpropiophenone.

By the action of magnesium naphthyl bromide on benzylideneacetophenone bromide, *naphthylphenylpropiophenone* is obtained, which crystallises in needles, melts at 121°, and is readily soluble in ether or alcohol.

When α-bromodiphenylpropiophenone is treated with an ethereal solution of magnesium phenyl bromide, diphenylpropiophenone and diphenyl are produced. If, however, the mixture is treated with benzoyl chloride before the addition of water, benzoyltriphenylpropenol is obtained. E. G.

Pinacone-Pinacolin Rearrangement. SALOMON F. ACREE (*Amer. Chem. J.*, 1905, **33**, 180—195. Compare Abstr., 1904, i, 742, 747).—When dihydroxydiphenyldihydrophenanthrene is heated with acetyl chloride, diphenylphenanthrone, $\begin{array}{l}C_6H_4\cdot CO \\ | \qquad\ \ | \\ C_6H_4\cdot CPh_2\end{array}$, is produced, which melts at 198° and is not easily oxidised by chromic acid (compare Werner and Grob, Abstr., 1904, i, 865). When this substance is heated with alcoholic potassium hydroxide at 150—190° for 6 hours, an *acid*, probably $CHPh_2\cdot C_6H_4\cdot C_6H_4\cdot CO_2H$, is formed which melts at 180—190°.

By the action of magnesium phenyl bromide on acenaphthenequinone, *dihydroxydiphenyldihydroacenaphthene*, $C_{10}H_6<\begin{array}{l}CPh\cdot OH \\ | \\ CPh\cdot OH\end{array}$, is obtained, which crystallises from alcohol or glacial acetic acid, melts at 154°, and when heated with acetyl chloride remains unchanged.

When *s*-diphenyldi-*p*-tolylpinacone (Acree, Abstr., 1904, i, 743) is heated with acetyl chloride for 10 hours, a *substance* is produced which is probably identical with the β-di-*p*-tolyldiphenylpinacolin described by Thörner and Zincke (Abstr., 1878, i, 223).

By the action of magnesium phenyl bromide on ethyl oxalate, β-benzopinacolin is not produced, but benzopinacone only is obtained (compare Dilthey and Last, Abstr., 1904, i, 667).

Tetraphenyltetramethylene glycol (Dilthey and Last, *loc. cit.*) melts at 206°. When ethyl succinate is treated with a boiling ethereal solution of magnesium phenyl bromide, a *substance*, probably tetraphenyltetramethylene oxide, $\begin{array}{l}CH_2\cdot CPh_2 \\ | \\ CH_2\cdot CPh_2\end{array}>O$, is formed, which crystallises from alcohol, melts at 163—165°, and slowly decolorises solution of bromine.

By the action of magnesium ethyl iodide on benzoin, $\alpha\beta$-diphenylbutylene $\alpha\beta$-glycol, OH·CPhEt·CHPh·OH, is produced, which melts at 115—116° and is only very slowly attacked by bromine.

Diphenyl-*m*-tolylcarbinol (Bistrzycki and Gyr, Abstr., 1904, i, 498) boils at 255° under 26 mm. pressure and melts at 65°. E. G.

Behaviour of Tetrabromo-*o*-benzoquinone towards Ketones and Aldehydes. C. Loring Jackson and F. W. Russe (*Ber.*, 1905, **38**, 419—421. Compare Abstr., 1904, i, 254).—Tetrabromo-*o*-benzoquinone does not combine with ketones and aldehydes to form compounds similar to those obtained from alcohols, but is converted by them into a mixture of hexabromo-*o*-quinocatechol ether,

$$C_6Br_4O_2{:}C_6Br_2O_2,$$

hexabromodihydroxycatechol ether, $C_6Br_4O_2{:}C_6Br_2(OH)_2$, and *heptabromo-o-quinocatechol hemiether*, $OH{\cdot}C_6Br_4O{\cdot}C_6Br_3O_2,1\frac{1}{2}C_6H_6$. The last compound crystallises from benzene in large, flat, yellow prisms, which lose benzene on exposure to air. It dissolves in ether, chloroform or nitrobenzene without decomposition; the alcoholic solution decomposes on warming and deposits hexabromo-*o*-quinocatechol ether. The hexabromo-compound is best prepared from tetrabromo-*o*-benzoquinone and acetone in the presence of benzene at the ordinary temperature, the reaction being completed in two weeks. When an excess of acetone is employed and the benzene is omitted, the two first-named compounds are chiefly obtained. Some bromoacetone is also produced, and when acetophenone is employed ω-bromoacetophenone is obtained. C. H. D.

Action of Potassium Iodide on Bromanil and Chloranil. Henry A. Torrey and W. H. Hunter (*Ber.*, 1905, **38**, 555—556).—When heated with potassium iodide in acetone solution, bromanil forms *dibromodi-iodo-*p*-benzoquinone*, $C_6O_2Br_2I_2$, which crystallises in reddish-brown prisms or golden plates, commences to sublime at about 240°, melts at about 255°, is easily soluble in benzene, toluene, hot acetone, or ethyl acetate, but only slightly so in alcohol, ether, or light petroleum; it dissolves in hot aqueous sodium hydroxide to a purple solution, and is easily reduced to the colourless *quinol*. With sodium phenoxide in aqueous solution, the quinone forms a *phenoxy*-derivative, with diphenylamine, in light petroleum solution, an *additive* compound, $C_6O_2Br_2I_2,NHPh_2$, which separates in dark red crystals, and with *o*-toluidine a similar *additive* compound. The action of powdered potassium iodide on chloranil, partly dissolved in acetone, leads to the formation of a green *substance*, which contains potassium, and when treated with water yields a yellow, insoluble *compound* and a purple solution. Under the same conditions, bromanil yields a similar derivative. G. Y.

2-Nitro-3 : 6-dihydroxy-*p*-benzoquinone-5-sulphonic Acid. Rudolf Nietzki and Alfred Humann (*Ber.*, 1905, **38**, 453—454).—Potassium 3 : 6-dichloroquinol-2 : 5-disulphonate, prepared by the

action of potassium sulphite on chloranil, reacts on warming with potassium nitrite to form *potassium 2-nitro-3 : 6-dihydroxy-p-benzoquinone-5-sulphonate*, $NO_2 \cdot C_6O_2(OK)_2 \cdot SO_3K$, which crystallises from water in yellow needles. The acid may be regarded as nitranilic acid in which one nitro-group is replaced by a sulpho-group. Silver nitrate precipitates a yellow, crystalline *potassium silver* salt, $C_6O_9NSKAg_2$. Stannous chloride reduces the potassium salt, yielding *2-amino-3 : 6-dihydroxyquinol-5-sulphonic acid hydrochloride*,

$$NH_2 \cdot C_6(OH)_4 \cdot SO_3H,HCl,$$

which forms colourless crystals, becoming brown on exposure to air. It was not found possible to break down the ring by oxidation.

C. H. D.

Dissociation of Phenoquinone and Quinhydrone. HENRY A. TORREY and H. HARDENBERGH (*Amer. Chem. J.*, 1905, **33**, 167—179. Compare Biltris, Abstr., 1899, i, 199).—As a preliminary to the study of the dissociation of phenoquinone, the molecular weights in benzene solution of its dissociation products, phenol and quinone, were determined. Determinations of the molecular weight of phenol by the ebullioscopic method gave results which show that this substance is somewhat polymerised at the boiling point of benzene, and determinations by the cryoscopic method confirmed the conclusions of Beckmann (Abstr., 1889, 11), Auwers (Abstr., 1894, ii, 133), and others that phenol is polymerised even at low concentrations, and that the polymerisation increases with the concentration. The average value obtained for the molecular weight of quinone by the boiling point method was 116, and by the freezing point method 105. The results of the cryoscopic determinations agree with those obtained by Auwers (*loc. cit.*), and show that the molecular weight of quinone is not affected by the concentration.

Determinations of the molecular weight of phenoquinone by both methods have shown that this substance is highly dissociated in benzene solution ; Biltris (*loc. cit.*) has found that this is also the case in ethereal solution. When phenol is added to a saturated solution of phenoquinone, a considerable quantity of phenoquinone separates, showing that phenol and quinone are the dissociation products. The action of these dissociation products on dissolved phenoquinone was studied by both ebullioscopic and cryoscopic methods. The results of these experiments are tabulated, and show that by the addition of one of the dissociation products to the dissociated phenoquinone solution a re-association takes place.

A determination of the molecular weight of quinhydrone in benzene solution has shown that the substance is completely dissociated into quinone and quinol, as Biltris (*loc. cit.*) has shown is the case in ethereal solution. If quinhydrone is dissolved in warm chloroform and the solution is slowly cooled, quinol separates at about 35°. As in the case of phenoquinone, quinhydrone may be precipitated from its solution by the addition of one of its dissociation products.

The yellow colour of solutions of phenoquinone and quinhydrone in various organic solvents shows that, in general, both substances are dissociated.

E. G.

vic-m-Xylenol and Tetramethyldiphenoquinone. KARL AUWERS and TH. VON MARKOVITS (*Ber.*, 1905, **38**, 226—237).—3 : 5 : 3′ : 5′-*Tetramethyldiphenoquinone*-4 : 4′, $C_{12}H_4Me_4O_2$, is best prepared by oxidising *vic-m*-xylenol dissolved in glacial acetic acid with chromic anhydride. Within 15—20 minutes, the quinone separates in glistening needles; crystallised from nitrobenzene or xylene, it separates in dark red needles and melts when fairly quickly heated at 210°. The quinone is also obtained when other oxidising agents are employed, as, for example, ferric salts, but the chromic anhydride method gives the best results. Hydroxylamine and phenylhydrazine act as reducing agents; the quinone is best reduced by the action of zinc-dust on the suspension in boiling acetic acid. The quinol, 3 : 5 : 3′ : 5′-*tetramethyl*-4 : 4′-*diphenol*, $C_{12}H_4Me_4(OH)_2$, so obtained, crystallises in colourless glass, glistening needles and flat prisms melt-at 220—221°; the *diacetate* separates from acetic acid in long needles melting at 174—175°. The diphenol is very easily reoxidised to the quinone, especially in alkaline solution, a *quinhydrone* being formed as an intermediate product; this crystallises in dark steel-blue plates melting at 201°. 2-*Chloro*-3 : 5 : 3′ : 5′-*tetramethyl*-4 : 4′-*dihydroxydiphenyl*, $OH\cdot C_6HClMe_2\cdot C_6H_2Me_2\cdot OH$, prepared by the action of concentrated hydrochloric acid on the quinone, crystallises in needles melting at 203°.

It is shown that only those phenols in which both the ortho-positions relative to the hydroxyl group are occupied and both the meta- and para-positions are free undergo easy oxidation to diphenoquinone derivatives in this manner. Further, the analogy between tetramethyldiphenoquinone and coerulignone (tetramethoxydiphenoquinone) is pointed out (compare Liebermann, Abstr., 1873, 1033; Hofmann, Abstr., 1878, 417, and Herzig and Pollak, Abstr., 1904, i, 808, 876). E. F. A.

Alizarin Dimethyl Ether. CARL GRAEBE (*Ber.*, 1905, **38**, 152—153. Compare Abstr., 1902, i, 42).—The action of methyl sulphate on deoxyalizarin in alkaline solution leads to the formation of the *dimethyl ether*, $C_6H_4<\begin{matrix}CH_2\cdot C{:}C(OMe)\cdot C\cdot OMe\\ CO-C{:}CH\text{———}CH\end{matrix}$, which crystallises in golden needles, melts at 150°, is easily soluble in alcohol, dissolves in concentrated sulphuric acid to a reddish-yellow solution, and is oxidised by sodium chromate and glacial acetic acid to *alizarin dimethyl ether*, $C_{16}H_{12}O_4$. This crystallises in golden needles, melts at 215°, is easily soluble in benzene or chloroform, and moderately so in hot alcohol, and dissolves in concentrated sulphuric acid to a red solution. It is identical with the dimethyl ether obtained from 1-nitro-2-methoxyanthraquinone (Farbwerke vorm. Meister, Lucius, & Brüning). G. Y.

Action of Alcoholic Potassium Hydroxide on Phenanthraquinone. RICHARD MEYER and OSKAR SPENGLER (*Ber.*, 1905, **38**, 440—450).—In the preparation of diphenic acid by the action of alcoholic potassium hydroxide on phenanthraquinone, a yellow sub-

stance is first obtained, and is converted into diphenic acid by prolonged boiling. The alcohol takes part in the reaction, the yellow compound not being obtained in aqueous or methyl alcoholic solution. The same compound is obtained by heating phenanthraquinone and glycollic acid in methyl alcoholic solution, $C_{14}H_8O_2 + C_2H_4O_3 = C_{16}H_8O_3 + 2H_2O$. It is the *lactone* of 10-*hydroxyphenanthryl*-9-*glyoxylic acid*,

$$\begin{array}{l} C_6H_4\cdot C\cdot CO \\ | \qquad \| \\ C_6H_4\cdot C-O \end{array} \!\!>\! CO,$$

which crystallises from organic solvents in orange needles and melts and decomposes at 220—221°. It dissolves in alkalis to yellow solutions, from which it is reprecipitated by acids. The *barium* salt, $C_{16}H_8O_4Ba$, forms pale yellow, felted needles. The *phenylhydrazone* forms reddish-yellow needles and melts and decomposes at 254°.

Zinc dust reduces the lactone in alkaline solution to *diphenylene-dihydrofuran*, $\begin{array}{l} C_6H_4\cdot C\cdot CH_2 \\ | \qquad \| \\ C_6H_4\cdot C-\!\!-O \end{array}\!\!>\!CH_2$, which crystallises from dilute acetic acid in long, flat needles and melts at 152°.

When fused, the lactone evolves carbon monoxide and carbon dioxide, forming a mixture of the *compounds* $\begin{array}{l} C_6H_4\cdot C\cdot CO\cdot C\cdot C_6H_4 \\ | \qquad \| \qquad\quad \| \quad | \\ C_6H_4\cdot C\cdot CO\cdot C\cdot C_6H_4 \end{array}$ and $\begin{array}{l} C_6H_4\cdot C\cdot CO\cdot C\cdot C_6H_4 \\ | \qquad \| \qquad\quad \| \quad | \\ C_6H_4\cdot C-O-C\cdot C_6H_4 \end{array}$.

C. H. D.

A Synthesis of Menthone and Menthol. ALBIN HALLER and CAMILLE MARTINE (*Compt. rend.*, 1905, **140**, 130—132).—3-Methyl-6-*iso*propyl*cyclo*hexanone, prepared by the action of *iso*propyl iodide on the sodium derivative of optically active 3-methyl*cyclo*hexanone (this vol., i, 214), boils at 207—209°, has a sp. gr. 0·9008 to 0·9017 at 17°, and $[\alpha]_D$ +12°56′ to 8°52′, and is a mixture of *d*- and *l*-menthone yielding an oxime, a semicarbazone, and a condensation product with benzaldehyde, which are respectively identical with the corresponding derivatives of menthone; on reduction with sodium in absolute alcohol, it is converted into menthol, m. p. 42—43°, which combines with phthalic acid to form a menthyl hydrogen phthalate melting at 120°.

M. A. W.

Cinnamylidenecamphor and its Reduction Products. HANS RUPE and GUNNAR FRISELL (*Ber.*, 1905, **38**, 104—122).—Cinnamylidenecamphor, $C_8H_{14}\!<\!\begin{array}{l} CO \\ | \\ C{:}CH\cdot CH{:}CHPh \end{array}$, was described by Haller (Abstr., 1891, 1498) as an uncrystallisable oil, but when prepared from sodium camphor and cinnamaldehyde in toluene suspension it may be obtained in a solid form, and then crystallises from alcohol in yellow, amber-like, rhombic crystals, $[a : b : c = 0·84856 : 1 : 1·8632]$ insoluble in water, dissolving readily in ether, benzene, or chloroform. It melts at 88—89° and boils at 227—228·5° under 11 mm. pressure and at 159° in the vacuum of the cathode light; $[\alpha]_D$ was found to be +269·74° in benzene and +296·11° in chloroform.

Sodium amalgam reduces cinnamylidenecamphor in methyl alcoholic

solution to *γ-phenylpropylcamphor*, $C_8H_{14}<\begin{matrix}CO\\ |\\ CH\cdot CH_2\cdot CH_2\cdot CH_2Ph\end{matrix}$, boiling at 200° under 11 mm. pressure and dissolving readily in organic solvents. It has a sp. gr. 1·0064 at 20°/4°; n_D 1·5242; $[\alpha]_D$ +66·53° in chloroform. Potassium permanganate oxidises it to benzoic and camphoric acids. It does not yield additive products with bromine or hydrogen bromide.

On heating cinnamylidenecamphor with a cold saturated solution of hydrogen bromide in glacial acetic acid at 100°, an oily product is obtained, consisting of a mixture of a bromo-acid and a brominated hydrocarbon. Zinc dust and acetic acid reduce it. The reduction product contains *phenylbutadienyltrimethyl*cyclo*pentane*,

$$C_5H_6Me_3\cdot CH{:}CH\cdot CH{:}CHPh,$$

a colourless, uncrystallisable oil boiling at 180° under 10 mm. pressure, and having a sp. gr. 0·9995 at 20°/4°, n_D 1·54089, and $[\alpha]_D$ +3·86°. The second reduction product is *phenylbutenyl-* or *phenylbutadienyl-trimethyl*cyclo*pentenecarboxylic acid*,

$$CHPh{:}CH\cdot CH{:}CH\cdot C_5H_5Me_3\cdot CO_2H,$$

which boils at 236—238° under 12 mm. pressure and has a sp. gr. 1·0007 at 20°/4° and n_D 1·52901.

Zinc dust and acetic acid reduce cinnamylidenecamphor, and the product may be separated by crystallisation from alcohol, followed by fractional distillation of the uncrystallisable portion into four fractions, the first two of which yield on crystallisation geometrically isomeric forms of *diphenylpropylenedicamphor*,

$$\begin{array}{r}C_8H_{14}<\begin{matrix}CO\\ |\\ C\cdot CH_2\cdot CH{:}CHPh\end{matrix}\\ |\qquad\qquad\quad\\ CHPh{:}CH\cdot CH_2\cdot \begin{matrix}C-\\ |\\ CO\end{matrix}>C_8H_{14}\end{array}\qquad\qquad \begin{array}{l}C_8H_{14}<\begin{matrix}CO\\ |\\ C\cdot CH_2\cdot CH{:}CHPh.\end{matrix}\\ \quad\qquad |\\ C_8H_{14}<\begin{matrix}C\cdot CH_2\cdot CH{:}CHPh\\ |\\ CO\end{matrix}\end{array}$$

trans-. *cis-*.

The trans-*modification* crystallises from alcohol in white leaflets, melts at 188°, dissolves readily in ether, benzene or chloroform, and has $[\alpha]_D$ +40·63°. The cis-*modification* crystallises in microscopic leaflets, melts at 152°, dissolves readily in organic solvents, and has $[\alpha]_D$ +30·22°. Both forms react with bromine in chloroform solution to form a *dibromo*-derivative, $C_{38}H_{44}O_2Br_2$, a yellow, crystalline powder melting at 118°, which yields the *trans*-compound on reduction. Both the *cis-* and *trans*-compounds combine with hydrogen bromide in glacial acetic acid solution, yielding a mixture of an *α-hydrobromide*, $C_{38}H_{48}O_2Br_2$, melting at 168°, and a *β-hydrobromide* melting at 215° and dissolving more readily in organic solvents than the α-isomeride.

Zinc dust and acetic acid reduce the α-hydrobromide to trans-*di-γ-phenylpropyldicamphor*, $C_{38}H_{50}O_2$, which crystallises from alcohol in small cubes and melts at 162°. In similar manner, the β-hydrobromide yields on reduction cis-*di-γ-phenylpropyldicamphor*, which separates from alcohol as a white, crystalline powder and melts at 205°. Both isomerides are stable towards potassium permanganate, bromine, and hydrogen bromide.

The third fraction from the reduction of cinnamylidenecamphor is

an uncrystallisable oil. The last fraction contains a *compound*, $C_{38}H_{46}O_3$, which crystallises from alcohol in white, silky needles and melts at 250°. C. H. D.

Transformation of Carvone and Eucarvone into Carvacrol and the Velocity of this Transformation. T. M. M. DORMAAR (*Rec. trav. chim.*, 1904, **23**, 394—400).—The measurements were made by heating solutions of the ketones in acetic acid with phosphoric oxide at 205° and observing the changes in specific gravity which took place. In the case of carvone, an attempt was made to use the change of specific rotation as a criterion of the progress of transformation, but this method was abandoned owing to the production of a small amount of colouring matter which interfered with the accuracy of the readings.

The reaction in both cases was unimolecular; the mean value of k in the case of the carvone transformation was 0·038, and for that of eucarvone 0·019. T. A. H.

Oximes of Pulegone. FRIEDRICH W. SEMMLER (*Ber.*, 1905, **38**, 146—148. Compare Beckmann and Pleissner, Abstr., 1891, 936; Wallach, Abstr., 1896, i, 309; Harries and Roeder, Abstr., 1900, i, 182).—*Pulegone dioxime*,

$$CHMe{<}{\begin{matrix}CH_2\cdot C(NOH)\\ CH_2 \text{——} CH_2\end{matrix}}{>}CH\cdot CMe_2\cdot NH\cdot OH,$$

is obtained when the alcoholic-ethereal solution of the product of the action of hydroxylamine, according to Beckmann's method, on pulegone is extracted with a small quantity of concentrated aqueous sodium hydroxide and carbon dioxide passed through the alkaline extract. It melts at 118° and is reduced, by sodium and alcohol, to 3 : 8-*diaminomenthane*, $CHMe{<}{\begin{matrix}CH_2\cdot C(NH_2)\\ CH_2 \text{——} CH_2\end{matrix}}{>}CH\cdot CMe_2\cdot NH_2$, which boils at 118—121° under 10 mm. pressure and has a sp. gr. 0·956 at 20°, and n_D 1·489; the *thiocarbamide* derivative, $C_{24}H_{32}N_4S_2$, melts at 157°. The action of nitrous acid on the sulphate of the base in aqueous solution leads to the formation of the *glycol*, $C_{10}H_{20}O_2$, which boils at 146—148° under 10 mm. pressure and is converted by the action of dilute sulphuric acid into *iso*pulegol. When distilled, the hydrochloride of 3 : 8-diaminomenthane yields hydrocarbons and a *base*,

$$\begin{matrix}CHMe\cdot CH_2\cdot CH\cdot NH\\ | \qquad\qquad | \qquad | \\ CH_2 - CH_2\cdot CH\cdot CMe_2\end{matrix} \ (?),$$

which boils at 65° under 15 mm. pressure and forms an insoluble *picrate* melting at 130°. G. Y.

Camphene, Camphenylone, *iso*Borneol, and Camphor. LOUIS BOUVEAULT and GUSTAVE BLANC (*Compt. rend.*, 1905, **140**, 93—95).—Methylcamphenylol, obtained by Wagner, Moycho, and Zienkowski by the action of magnesium methyl iodide on camphenylone (Abstr., 1904, i, 438), behaves as a tertiary alcohol on boiling with pyruvic acid (compare Bouveault, Abstr., 1904, i, 465), the main product of the reaction being camphene, which reacts with the pyruvic acid to form *iso*bornyl pyruvate, boiling at 133—134° under 11 mm. pressure, and yielding a

semicarbazone melting at 214° or 221° according to the rate of heating. *iso*Borneol, on the contrary, behaves as a primary or secondary alcohol when heated with pyruvic acid, forming a pyruvate the semicarbazone of which is identical with the one already described. M. A. W.

Green Colour of Kajeput Oil. H. C. Prinsen Geerligs (*Chem. Centr.*, 1905, **1**, 95; from *Chem. Weekblad*, 1904, **1**, 931—934).—The green colour of the oil is due to the presence of copper, this being dissolved by the butyric and valeric acids and the esters of these which are contained in the oil. This was shown by experiments with the purified oil from which the acids and esters had been completely removed. This purified oil, after addition of water and either ethyl formate, acetate, propionate, butyrate, valerate, lactate, citrate, oxalate or cinnamate and a small quantity of the corresponding acid, was treated with copper shavings. The butyrate and valerate mixtures were the only ones which developed a green colour, the copper dissolving in the aqueous layer in all the other cases.

Valerian oil also dissolves copper, and, as in the case of kajeput oil, the green colour cannot be removed by shaking out with water.

H. M. D.

Peppermint Oil from Java. P. Van der Wielen (*Chem. Centr.*, 1905, **1**, 95; from *Pharm. Weekblad*, 1904, **41**, 1081—1084).—Examination of an essential oil obtained from *Mentha javanica* gave the following data. It was light green in colour, had a bitter taste and an odour resembling peppermint. Sp. gr. $=0{\cdot}9214$ at 15°; $a_D+4°40'$ at 20° in a 100 mm. tube. It dissolved in one and a half times its volume of 70 per cent. alcohol. After cooling to $-60°$, it became entirely liquid again at $-15°$. It contained a considerable amount of pulegone, but little or no menthol or menthone. H. M. D.

Varieties of Caoutchouc. Weber's Dinitrocaoutchouc. Carl D. Harries (*Ber.*, 1905, **38**, 87—90. Compare Abstr., 1902, i, 811; 1903, i, 189, 642; 1904, i, 757, 1038; Weber, Abstr., 1902, i, 552; 1903, ii, 762).—The properties of Weber's compound of caoutchouc with nitric peroxide vary with the time during which the reagent is allowed to act. When rapidly prepared in benzene solution, the product is a yellow, sandy powder, decomposing at about 90°, insoluble in benzene, alcohol, ethyl acetate, chloroform, or carbon disulphide, but dissolving in nitrobenzene, aniline, pyridine, or quinoline on warming. When the product is allowed to remain 20 hours before filtering, it becomes soluble in ethyl acetate or acetone and decomposes at 157—160°. Its properties resemble those of Weber's compound, but the composition differs from the formula $C_{10}H_{16}O_4N_2$, assigned by him, and approaches that of the author's nitrosite, $C_{10}H_{15}O_7N_3$.

C. H. D.

Caoutchouc Nitrosite and its Use for the Analysis of Crude Caoutchoucs and Caoutchouc Products. I. Paul Alexander (*Ber.*, 1905, **38**, 181—184).—According to Weber (Abstr., 1902, i, 552), a compound $C_{10}H_{16}O_4N_2$ is formed when a mixture of

nitrogen peroxide and oxygen is passed into caoutchouc solutions. The author, in amplification of earlier work (compare Abstr., 1904, i, 905), has now examined a considerable number of samples of caoutchouc from various sources according to Weber's method, but the products obtained did not possess the composition $C_{10}H_{16}O_4N_2$.

The figures for the analyses made agreed better for those of Harries' nitrosite "c" than for Weber's compound. A. McK.

African Copals. Ch. Coffignier (*Bull. Soc. chim.*, 1905, [iii], **33**, 169—176).—Three West African resins known commercially as Kissel, Cameroon, and Accra copals are described. Kissel copal melts at 110°, has a sp. gr. 1·066 at 27°, acid number 70·4, Köttstorfer number 117·8, and is soluble in excess of boiling alcohol to the extent of 50 per cent.

Cameroon copal melts at 150°, has a sp. gr. 1·052 at 27°, acid number 159·7, Köttstorfer number 70·0, and is soluble to the extent of 45 per cent. in excess of boiling alcohol.

Accra copal melts at 120°, has a sp. gr. 1·033 at 27°, acid number 97·8, Köttstorfer number 140, and is soluble in excess of boiling alcohol to the extent of 90 per cent. The solubilities of the three copals in twelve different solvents are tabulated in the original.

T. A. H.

Decomposition Products of a Derivative of Artemisin (1 : 4-Dimethyl-β-naphthol and Propionic Acid). Pasquale Bertolo (*Gazzetta*, 1904, **34**, ii, 322—326. Compare Abstr., 1902, i, 814, and 1904, i, 177).—When fused with potassium hydroxide, the product of the reduction of artemisin by stannous chloride and hydrochloric acid yields 1 : 4-dimethyl-β-naphthol (*loc. cit.*) and propionic acid. It hence behaves quite like the desmotroposantonins, but does not, like the latter, yield santonous acids on reduction with zinc dust and acetic acid. When, however, this reduction product of artemisin is subjected to reduction by Ladenburg's method, it yields a substance which is probably the corresponding acid, and is to be further investigated. Artemisin hence contains the same fundamental nucleus as santonin united to a propionic acid residue. T. H. P.

[Theory of Dyeing.] Wilhelm Biltz (*Ber.*, 1905, **38**, 184—187).—Polemical. A reply to Zacharias (this vol., i, 75). A. McK.

Researches in the Furan Series. R. Marquis (*Ann. Chim. Phys.*, 1905, [viii], **4**, 196—288).—The paper is mainly a *résumé* of work already published (compare Abstr., 1900, i, 798; 1901, i, 222; 1902, i, 302, 483; 1903, i, 49, 370, 644; 1904, i, 82). The aldehyde obtained by the action of water on nitrosuccinaldehyde monoacetin (Abstr., 1902, i, 483) has been identified as maleic dialdehyde, and the following derivatives prepared: (1) a *diphenylhydrazone*, melting at 236—237°, by Maquenne's metallic block method, and yielding, on oxidation, the *tetrazone*, $\begin{matrix} CH\cdot CH:N\cdot NPh \\ \| \qquad\qquad\quad | \\ CH\cdot CH:N\cdot NPh \end{matrix}$, crystallising in scales of a magnificent red colour with a green reflex and melting at 174—175°;

(2) the *dioxime*, $\begin{matrix} CH\cdot CH:NOH \\ \| \\ CH\cdot CH:NOH \end{matrix}$, decomposing at 220° and yielding a *dibenzoyl* derivative melting at 165°. M. A. W.

Beckmann's Rearrangement in Oximes of Ketone-alcohols of the Benzoin Type. ALFRED WERNER and TH. DETSCHEFF (*Ber.*, 1905, **38**, 69—84. Compare Werner and Piguet, this vol., i, 66).—In the preparation of α-benzoinoxime by Goldschmid and Polanovska's method (Abstr., 1887, 492), the β-oxime is simultaneously produced, and a method for the separation of the oximes is described.

Acetyl-α-benzoinoxime, OAc·N:CPh·CHPh·OH, separates from warm alcohol in colourless, granular crystals and melts at 112°. *Acetyl-β-benzoinoxime* forms long, flat prisms and melts at 111°. Chromic acid oxidises the β-compound in acetic acid solution at 40—50° to acetyl-γ-benziloxime, thus confirming the configurations already assigned (*loc. cit.*). The α-compound is not attacked.

Phenylcarbimide combines with both oximes in ethereal solution with development of heat. The *α-compound* separates from warm ether in white crystals and melts at 124°; the *β-compound* crystallises from dilute alcohol in feathery groups of silky needles and melts at 120°.

In the preparation of α-furoinoxime (Macnair, Abstr., 1890, 1245), *β-furoinoxime* is produced at the same time, and separates from ether in slightly yellow groups of crystals melting at 102°. Furoin is much more readily converted into the oximes than benzoin.

The Beckmann rearrangement of the furoinoximes proceeds with difficulty when phosphorus pentachloride is used, more readily with benzenesulphonic chloride. In both cases, a rearrangement of the second type occurs, the α-oxime yielding a nitrile and the β-oxime a carbylamine. Pyromucic acid was obtained on hydrolysing the nitrile with dilute sulphuric acid.

Acetyl-α-furoinoxime, $C_{12}H_{11}O_5N$, separates from benzene in granular crystals and melts at 113°; *acetyl-β-furoinoxime* forms groups of needles and melts at 108°. The acetyl group is removed on warming with alcohol.

Phenylcarbimide combines with the furoinoximes, the *α-compound*, $C_{17}H_{14}O_5N_2$, forming colourless, star-shaped crystals melting at 56° and becoming dark in air; the *β-compound* forms needles melting at 120°.

Benzofuroin, COPh·CH(OH)·C_4OH_3, reacts with hydroxylamine in alkaline solution to form a mixture of *α-benzofuroinoxime*, crystallising from alcohol in small prisms melting at 160°, and *β-benzofuroinoxime*, which crystallises with difficulty, but forms transparent crystals containing ether, which break up at 35° and then melt at 90°. With benzenesulphonic chloride, the α-oxime yields benzaldehyde and furfuronitrile; the β-oxime yields a carbylamine. This determines the following configuration for the oximes:

$$\alpha.\ \begin{matrix} OH\cdot CHPh\cdot C\cdot C_4OH_3 \\ \| \\ OH\cdot N \end{matrix}\ ; \qquad \beta.\ \begin{matrix} OH\cdot CHPh\cdot C\cdot C_4OH_3 \\ \| \\ N\cdot OH \end{matrix}.$$

Acetyl-α-benzofuroinoxime, $C_{14}H_{13}O_4N$, crystallises from benzene and

melts at 115°; *acetyl-β-furoinoxime* forms needles and melts at 96°.

The *compound* of phenylcarbimide with α-benzofuroinoxime, $C_{19}H_{16}O_4N_2$, forms an uncrystallisable syrup; the *β-compound* crystallises from dilute alcohol and melts at 138°.

In each pair of oximes here studied, the α-isomeride, in which the hydroxyl and CHR·OH groups occupy the *cis*-position, has a higher melting point and is less soluble than the β-oxime.

C. H. D.

Derivatives of Dihydro*iso*benzofuran. ALFRED GUYOT and J. CATEL (*Compt. rend.*, 1905, **140**, 254—256. Compare Haller and Guyot, Abstr., 1904, i, 660).—Methylphthalate or methyl *o*-benzoylbenzoate react with magnesium phenyl bromide to give *2-hydroxy-1 : 1 : 2-triphenyl-1 : 2-dihydro*iso*benzofuran*, $C_6H_4<\genfrac{}{}{0pt}{}{CPh_2}{CPh\cdot OH}>O$, melting at 118°, and the same compound is obtained by the condensation of magnesium phenyl bromide with diphenylphthalide according to the equation $C_6H_4<\genfrac{}{}{0pt}{}{CPh_2}{CO}>O + MgPhBr = C_6H_4<\genfrac{}{}{0pt}{}{CPh_2}{CPh(OMgBr)}>O \longrightarrow$

$$C_6H_4<\genfrac{}{}{0pt}{}{CPh_2}{CPh(OH)}>O.$$

The authors find that diphenylphthalide is formed as an intermediate compound in the first reactions, methyl phthalate yielding first benzoylbenzoic acid, and then diphenylphthalide, by the action of a small quantity of magnesium phenyl bromide, whilst methyl benzoylbenzoate yields diphenylphthalide and *o*-dibenzoylbenzene under similar conditions. 2-Hydroxy-1 : 1 : 2-triphenyl-1 : 2-dihydro*iso*benzofuran condenses readily with phenols or aromatic amines to give derivatives of the type $C_6H_4<\genfrac{}{}{0pt}{}{CPh_2}{CPh(C_6H_4R)}>O$, where R = ·$NMe_2$, ·$NH_2$, ·OH, &c., the compounds with dimethylaniline, phenol, and aniline melting at 177°, 167°, and 200° respectively, and is reduced by sodium amalgam in alcoholic solution, yielding *o-benzhydryltriphenylcarbinol*,

$$C_6H_4<\genfrac{}{}{0pt}{}{CPh_2\cdot OH}{CHPh\cdot OH},$$

melting at 150°. M. A. W.

9-Phenylxanthen. RICHARD MEYER (*Ber.*, 1905, **38**, 450—453. Compare Meyer and Saul, Abstr., 1893, i, 471; Ullmann and Engi, Abstr., 1904, i, 682).—9-Phenylxanthen, prepared by distilling fluoran with zinc dust, melts at 138—139°, and that prepared by reducing phenylxanthydrol at 144—145°. The two products resemble one another in all respects except the melting point. C. H. D.

Dibromo-additive Compounds of the Cinchona Alkaloids. A. CHRISTENSEN (*J. pr. Chem.*, 1905, [ii], **71**, 1—29. Compare Abstr., 1904, i, 184; Comstock and Koenigs, Abstr., 1892, 1010).—Two isomeric cinchonidine dibromides are formed by adding bromine to the alkaloid in hydrogen bromide and glacial acetic acid solution; α-cin-

chonidine dibromide crystallises out as the hydrobromide; the β-isomeride is precipitated from the mother liquor as the insoluble nitrate.

α-Cinchonidine dibromide crystallises in large, thin, rhombic, often hexagonal leaflets, blackens at about 200°, melts at about 225°, is optically inactive, and evolves only traces of hydrogen bromide when boiled with alcohol. The nitrate,

$$C_{19}H_{22}ON_2Br_2,2HNO_3,2H_2O,$$

crystallises in rosettes or sheaves of long, prismatic needles (Abstr., 1901, i, 481); the hydrobromide, $C_{19}H_{22}ON_2Br_2,2HBr,2H_2O$, forms a yellow powder consisting of microscopic prisms; the perbromide, $C_{19}H_{22}ON_2Br_2,2HBr,Br_2$, crystallises in yellow, quadratic leaflets; the *sulphate*, $(C_{19}H_{22}ON_2Br_2)_2,H_2SO_4,3H_2O$, crystallises in long needles or prisms, is almost insoluble in cold water, but dissolves easily in dilute sulphuric acid, with formation of an acid sulphate. When treated with concentrated sulphuric acid, α-cinchonidine dibromide forms a sulphonic acid, which crystallises in long, thin needles, evolves hydrogen bromide when boiled with alcoholic potassium hydroxide, and forms an insoluble nitrate, $C_{19}H_{21}ON_2Br_2\cdot SO_3H,HNO_3,H_2O$.

β-Cinchonidine dibromide crystallises in long prisms, blackens at about 200°, melts at about 210°, has $[\alpha]_D$ − 135° in 2·15 per cent. solution in a mixture of chloroform and alcohol, and, when boiled in 90 per cent. alcohol, is partly converted into bromocinchonidine. The *nitrate*, $C_{19}H_{22}ON_2Br_2,2HNO_3,H_2O$, crystallises in microscopic, rhombic plates or from boiling water in short prisms (compare Abstr., 1904, i, 520); the *hydrobromide*, $C_{19}H_{22}ON_2Br_2,2HBr,3H_2O$, crystallises in long, white, sharp needles; the *perbromide*, $C_{19}H_{22}ON_2Br_2,2HBr,Br_4,H_2O$ (?), crystallises in prisms and is reduced with aqueous sulphurous acid to β-cinchonidine dibromide; the *sulphate*,

$$(C_{19}H_{22}ON_2Br_2)_2,H_2SO_4,7H_2O\ (?),$$

crystallises in needles and at 100—105° is partly converted into the sulphonic acid; the insoluble *acid sulphate*, $C_{19}H_{22}ON_2Br_2,2H_2SO_4$, formed when an excess of sulphuric acid is added to the solution of the β-dibromide in dilute sulphuric acid, crystallises in thin, colourless hexagonal, rhombic leaflets. The *sulphonic acid*, formed by the action of concentrated sulphuric acid, does not form an insoluble nitrate or hydrobromide.

Both cinchonidine dibromides yield the same dibromocinchonidine and bromocinchonidine (Abstr., 1904, i, 520). Comstock and Koenigs' α- and β-cinchonine dibromides (Abstr., 1887, 281) are formed by the action of bromine on the alkaloid in hydrogen bromide and glacial acetic acid solution; the hydrobromide of the α-isomeride crystallises from the reaction solution, whilst the β-isomeride is precipitated on addition of ammonia to the mother liquors. α-Cinchonine dibromide crystallises in tufts of small leaflets and has $[\alpha]_D$ + 179·4° in 2·05 per cent. solution in a mixture of chloroform and alcohol. The *nitrate*, $C_{19}H_{22}ON_2Br_2,2HNO_3,H_2O$, crystallises in feathery aggregates of needles and is only slightly soluble in cold water; the hydro bromide, $C_{19}H_{22}ON_2Br_2,2HBr$, crystallises in long, prismatic needles or pointed prisms; the perbromide, $C_{19}H_{22}ON_2Br_2,2HBr,Br_2$, formed by the action of an excess of bromine on the α-dibromide in hydrogen bromide and glacial acetic acid solution, crystallises in microscopic-

yellow needles; the sulphate is only slightly soluble in water, but easily soluble in an excess of dilute sulphuric acid.

β-Cinchonine dibromide forms a granular, partly crystalline powder, has $[\alpha]_D$ $+107 \cdot 5°$ in 1 per cent. solution in a mixture of chloroform and alcohol, and, when boiled with alcohol, is partly converted into bromocinchonine. The *nitrate*, $C_{19}H_{22}ON_2Br_2,2HNO_3,H_2O$, crystallises in long, thin plates; the *hydrobromide*, $C_{19}H_{22}ON_2Br_2,2HBr$, forms small crystals resembling octahedra; the sulphate resembles the α-salt. Both cinchonine dibromides, when treated with alcoholic potassium hydroxide, yield the same bromocinchonine. G. Y.

Action of Methyl Iodide on the *iso*Nitroso-compounds of Cinchotoxine and Quinotoxine. GEORG ROHDE and G. SCHWAB (*Ber.*, 1905, **38**, 306—320. Compare von Miller and Rohde, Abstr., 1901, i, 95).—iso*Nitrosomethylcinchonine*,

$$N\!\lessdot\!\begin{matrix}C_6H_4\text{—}\\CH\cdot CH\end{matrix}\!\gtrdot C\cdot C(N\cdot OH)\cdot CO\cdot CMe\!\lessdot\!\begin{matrix}CH_2\text{————————}CH_2\\CH(CH:CH_2)\cdot CH_2\end{matrix}\!\gtrdot NMe,$$

obtained by the action of amyl nitrite and sodium ethoxide on methylcinchonine dissolved in absolute alcohol, crystallises from ethyl acetate in colourless prisms, melts at 158—159°, and is best purified through the *hydrochloride*, $C_{20}H_{24}O_2N_3Cl$, which separates from alcohol on adding chloroform in crystals containing the latter, and melts and decomposes at about 230°.

iso*Nitrosomethylcinchonine hydriodide*, $C_{20}H_{24}O_2N_3I$, resembles the hydrochloride in separating with chloroform of crystallisation, and melts and decomposes at about 180°.

iso*Nitrosomethylcinchonine methiodide*,

$$N\!\lessdot\!\begin{matrix}C_6H_4\text{—}\\CH\cdot CH\end{matrix}\!\gtrdot C\cdot C(N\cdot OH)\cdot CO\cdot CMe\!\lessdot\!\begin{matrix}CH_2\text{————————}CH_2\\CH(CH:CH_2)\cdot CH_2\end{matrix}\!\gtrdot NMe,MeI,$$

separates from methyl alcohol in slightly red crystals and melts and decomposes between 228° and 235°. iso*Nitrosocinchotoxine hydriodide*, $C_{19}H_{22}O_2N_3I$, prepared from *iso*nitrosocinchotoxine, melts at 85°, subsequently solidifies, and then melts and decomposes at 210°.

The methiodide, $C_{19}H_{21}O_2N_3,MeI$, described by von Miller and Rohde (*loc. cit.*), is really identical with the *iso*nitrosomethylcinchonine methiodide just described; this would explain the abnormal properties it was supposed to possess. The action of methyl iodide on *iso*-nitrosocinchotoxine thus gives rise to the methiodide and hydriodide of *iso*nitrosomethylcinchonine and to *iso*nitrosocinchotoxine hydriodide.

iso*Nitrosoquinotoxine hydriodide*, $C_{20}H_{24}O_3N_3I$, prepared by adding the requisite quantity of sodium acetate to a solution of the dihydriodide, melts at 102—105°, and, after solidification, at 217°. *iso*-Nitrosomethylquinine, prepared by the action of amyl nitrite on methylquinine, is identical with *iso*nitrosomethylquinotoxine (*loc. cit.*); it separates from benzene in wedge-shaped crystals containing benzene and melting at 69—71°, but when free from benzene it melts at 156°. The *hydriodide*, $C_{21}H_{26}O_3N_3I$, of *iso*nitrosomethylquinotoxine crystallises from alcohol and melts at 207°; the *methiodide*, $C_{22}H_{28}O_3N_3I$, crystallises from alcohol in slender needles or in nodules, and melts and decomposes at about 163°. The action of methyl iodide on *iso*nitroso-

quinotoxine dissolved in chloroform gives *iso*nitrosomethylquinotoxine methiodide and *iso*nitrosomethylquinotoxine hydriodide.

W. A. D.

Harmine and Harmaline. OTTO FISCHER and CHRISTIAN BUCK (*Ber.*, 1905, **38**, 329—335. Compare Abstr., 1901, i, 405).—When harminic acid is heated with concentrated hydrochloric acid for several hours at 190—200°, it loses only one carboxyl group and gives apo*harminecarboxylic acid*, which crystallises from hot water in slender needles or small plates and is both acid and basic in its properties; the *hydrochloride*, $C_9H_8O_2N_2,HCl$, *platinichloride*, and *aurichloride* are well defined substances. When heated at 330°, the acid loses carbon dioxide and gives *apo*harmine; towards reducing agents, for example, hydriodic acid or sodium in boiling amyl alcohol, the acid is very stable. *Methyl*apo*harminecarboxylic acid*, $C_{10}H_{10}O_2N_2$, prepared either by methylating *apo*harminecarboxylic acid or by heating methylharminic acid with concentrated hydrochloric acid at 190° for 2 hours, gives a *hydrochloride*, $C_{10}H_{10}O_2N_2,HCl,H_2O$, crystallising in colourless plates, and a *hydriodide*, $C_{10}H_{10}O_2N_2,HI$, crystallising in needles. *Nitro*apo*harminecarboxylic acid*, $C_9H_7O_4N_3$, prepared by direct nitration, crystallises from water in nearly colourless prisms and begins to decompose at about 190°. *Nitro*apo*harmine nitrate*,

$$C_8H_7O_2N_3,HNO_3,\tfrac{1}{2}H_2O,$$

crystallises in reddish-yellow, nodular aggregates. On methylation, nitro*apo*harmine gives *nitromethyl*apo*harmine*, $C_9H_9O_2N_3$, which crystallises from dilute methyl alcohol and decomposes at about 225°; the *hydriodide*, $C_9H_9O_2N_3,HI$, forms yellow leaflets, the *aurichloride* melts at 174°, and the *platinichloride*, with $2H_2O$, decomposes at 240—245°. Nitro*apo*harmine is not changed when boiled with chromic acid in acetic acid solution; on reduction with tin and hydrochloric acid, it gives *amino*apo*harmine*, which was isolated as the *platinichloride*,

$$C_8H_{11}N_3PtCl_6;$$

this crystallises in golden-yellow prisms and decomposes at 270°.

*Dihydro*apo*harmine picrate*, $C_8H_{10}O_2,C_6H_3O_7N_3$, is a crystalline salt which is of service in purifying the base.

When concentrated sulphuric acid is added to harmine dissolved in acetic anhydride, a *harmine*-N-*sulphonic acid*, $C_{13}H_{12}O_4N_2S$, is obtained, which crystallises in slender needles and is decomposed by boiling dilute hydrochloric acid, giving sulphur dioxide and harmine hydrochloride.

W. A. D.

Chloro-derivatives of Strychnine. GAETANO MINUNNI and F. FERRULLI (*Gazzetta*, 1904, **34**, ii, 364—373).—The following derivatives of the tetrachlorostrychnine obtained by Minunni and Ortoleva (Abstr., 1900, i, 309) have been prepared.

The *hydrochloride*, $C_{21}H_{18}O_2N_2Cl_4,2H_2O$, separates from acetic acid solution in white, acicular crystals, which are only slightly soluble in the ordinary solvents and begin to lose hydrogen chloride at 100°, although at 260° they are still unmelted. The free base ($+H_2O$) melts and decomposes at 165—170°. The *phenylhydrazone*,

$$C_{21}H_{18}ON_2Cl_4{:}N_2HPh,$$

separates from alcohol in minute, yellow crystals, which do not melt at 260° and are soluble in alcohol, benzene, or ethyl acetate and to a slight extent in ether. The *acetyl* derivative, $C_{21}H_{17}O_2N_2Cl_4Ac$, which is very readily soluble in ethyl acetate, and to a less extent in alcohol or benzene, begins to turn brown at about 140° and melts without decomposing at 180—197°. The *benzoyl* derivative, $C_{21}H_{17}O_2N_2Cl_4Bz$, separates from ether in crystals which turn brown at about 150°, blacken at 220°, and do not melt at 260°; it dissolves slightly in alcohol, and readily in ethyl acetate, benzene, or acetic acid. Another *benzoyl* derivative (with H_2O) was also prepared which separates from alcohol in pale yellow crystals softening at 130° and melting and decomposing at 150—155°; it is soluble in ether, alcohol, acetic acid, and ethyl acetate. The action of excess of acetyl chloride on tetrachlorostrychnine in pyridine solution yields *diacetyltrichlorostrychnine*, $C_{21}H_{15}O_2N_2Cl_3Ac_2$, which separates from ether or alcohol in white, acicular crystals melting and decomposing at 185° and dissolving in ethyl acetate or acetic acid. *Tetrachlorodinitrostrychnine*,

$$C_{21}H_{16}O_2N_2Cl_4(NO_2)_2,$$

is deposited from alcohol in microscopic crystals, which turn brown at about 170°, do not melt at 260°, and dissolve readily in acetic acid or ethyl acetate and to a slight extent in ether or benzene. T. H. P.

Action of Chlorine on Brucine in Glacial Acetic Acid Solution. Gaetano Minunni and R. Ciusa (*Gazzetta*, 1904, **34**, ii, 361—363).—By passing chlorine into a solution of brucine hydrate in glacial acetic acid, *hexachlorobrucine hydrochloride*,

$$C_{23}H_{20}O_4N_2Cl_6,HCl,$$

is obtained as a white, crystalline powder, turning red in the light, and dissolving in alcohol, ethyl acetate, ammonia, or potassium hydroxide solution, or in concentrated sulphuric acid with evolution of hydrogen chloride. The *base* is a white powder, which is turned yellow by light and is soluble in ether, benzene, alcohol, ethyl acetate, or chloroform. Both the base and its hydrochloride turn brown at about 120°, blacken at about 200°, and are still unmelted at 260°. They are not attacked by concentrated nitric acid.

By G. Coronedi. The hydrochlorides of tetrachlorostrychnine and hexachlorobrucine are non-poisonous and quite innocuous to dogs.

T. H. P.

8-Aminoparaxanthine and its Derivatives. C. F. Boehringer & Söhne (D.R.-P. 156901. Compare following abstract).—8-Chloroparaxanthine reacts with ammonia at 150—155° in alcoholic solution to form 8-*aminoparaxanthine*, $C_7H_7O_2N_4\cdot NH_2$, which blackens at 350° without melting. The *sodium* salt forms colourless needles. 8-*Methylaminoparaxanthine* sinters at 350° and melts and decomposes at 370°. 8-*Dimethylaminoparaxanthine* forms long needles and melts at 225°; the crystalline *sodium* salt dissolves readily in water. 8-*Anilinoparaxanthine* melts and decomposes at about 340°. C. H. D.

8-Aminotheophylline and its Alkyl and Aryl Derivatives. C. F. Boehringer & Söhne (D.R.-P. 156900).—8-Chlorotheophylline

reacts with ammonia or amines on heating in alcoholic solution at 150°, although less readily than 8-chlorocaffeine.

8-*Aminotheophylline*, $\begin{array}{l}\mathrm{NMe{\cdot}CO{\cdot}C{\cdot}NH} \\ \mid \qquad\quad\ \ \| \\ \mathrm{CO{\cdot}NMe{\cdot}C{-\!-}N}\end{array}\!\!>\mathrm{C{\cdot}NH_2}$, forms needles and becomes brown at 310°, slowly melting and decomposing. 8-*Anilinotheophylline* crystallises from alcohol in colourless needles and melts at 320°. 8-*Dimethylaminotheophylline* forms long needles and melts at about 330° to a colourless liquid. All these derivatives form salts with both acids and bases. C. H. D.

Attempt to Synthesise Hæmopyrrole. L. A. Tschugaeff and N. A. Schloesinger (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 1258—1268).—A close connection exists between hæmoglobin and chlorophyll, since both contain a pyrrole nucleus and both are capable of yielding hæmopyrrole under certain conditions. From the work of Küster (Abstr., 1900, i, 68; 1901, i, 58 and 298; 1902, i, 845), it seems probable that hæmopyrrole is 3-methyl-4-propylpyrrole. In an attempt to synthesise the latter compound, the author has prepared the following pyrrole derivatives.

2-Methyl-5-*iso*propylpyrrole (see Tiemann and Semmler, Abstr., 1897, i, 247) resembles hæmopyrrole in yielding a mercury compound, $(C_8H_{12}N)_2Hg,4HgCl_2$, but differs from it in its other reactions.

The interaction of ethyl sodiopropylmalonate and ethyl α-bromopropionate yields the *ester*, $CO_2Et{\cdot}CHMe{\cdot}CPr(CO_2Et)_2$, which boils at 276—282° and is a viscous liquid with the characteristic odour of polycarboxylic esters. Hydrolysis of this ester by means of sodium hydroxide yields *α-methyl-β-propylsuccinic acid*,

$$CO_2H{\cdot}CHMe{\cdot}CHPr{\cdot}CO_2H,$$

which crystallises from water in long needles melting at 156—157° and is readily soluble in alcohol, ether, and most other organic solvents; when gently heated, it sublimes. The *silver* salt of this acid, $C_6H_{12}(CO_2Ag)_2$, forms a heavy, curdy precipitate and the *ammonium* salt a micro-crystalline precipitate soluble in water; the *sodium*, *potassium*, *uranium*, *lead*, *copper*, and *iron* salts were prepared. On heating the ammonium salt for some time at its melting point and subsequently distilling under diminished pressure, it yields the corresponding *imide*, $\mathrm{NH}\!<\!\begin{array}{l}\mathrm{CO{\cdot}CMe} \\ \qquad\ \mid \\ \mathrm{CO{\cdot}CPr}\end{array}$, which boils at 167—168° under 20 mm. pressure and sets to a crystalline mass melting at 51—53°. The transformation of this imide into 3-methyl-4-propylpyrrole is attended with difficulty, the reaction being possibly brought about to some slight extent by heating the imide with phosphorus trisulphide or pentasulphide. T. H. P.

Ethyl 1-Camphyl-2:5-dimethylpyrrole-3:4-dicarboxylate and its Derivatives. Carl Bülow (*Ber.*, 1905, **38**, 189—193. Compare Knorr and Bülow, Abstr., 1884, 1381).—Ethyl diacetylsuccinate readily condenses with an acetic acid solution of camphylamine yielding *ethyl* 1-*camphyl*-2:5-*dimethylpyrrole*-3:4-*dicarboxylate*,

$$\begin{array}{l}\mathrm{CH{-\!-}CH_2} \\ \| \\ \mathrm{CMe{\cdot}CMe_2}\end{array}\!\!>\mathrm{CH{\cdot}CH_2{\cdot}CH_2{\cdot}N}\!<\!\begin{array}{l}\mathrm{CMe{:}C{\cdot}CO_2Et} \\ \qquad\quad \mid \\ \mathrm{CMe{:}C{\cdot}CO_2Et}\end{array},$$

which crystallises in large, glistening plates melting at 78°. It dissolves in most organic solvents, is odourless and tasteless, and on hydrolysis with aqueous alcoholic potash yields the *potassium* salt, from which the *acid* may be obtained by addition of acetic acid. The acid melts and decomposes at 204°, and on titration with standard potassium hydroxide in presence of phenolphthalein behaves as a monobasic acid. It dissolves readily in alcohol or acetic acid, but is reprecipitated on the addition of water, and is only sparingly soluble in benzene. The *ammonium* salt crystallises in colourless, slender needles, is readily soluble in hot water, and its solution yields precipitates with solutions of calcic, ferric, or cupric chlorides and with silver nitrate.

When heated at 204—210°, the acid is decomposed yielding 1-*camphyl*-2 : 5-*dimethylpyrrole* in the form of a viscid, yellow oil, which dissolves readily in most solvents. Its alcoholic solution, when warmed with ferric chloride solution, is turned an intense orange-yellow colour, and a pine shaving dipped in the solution gives a violet-red coloration with concentrated hydrochloric acid. J. J. S.

4-Methylpyridine. FELIX B. AHRENS (*Ber.*, 1905, **38**, 155—159). —The high boiling fraction of commercial "β-picoline" was added to the calculated amount of 30 per cent. alcoholic hydrochloric acid, when 2 : 6-dimethylpyridine hydrochloride separated, whilst from the filtrate the double salt of mercuric chloride and 4-methylpyridine was prepared. 3-Methylpyridine is as chemically active as the corresponding 1-compound.

4 : 4′-*Dimethyldipyridyl*, prepared by the action of sodium on 4-methylpyridine, was identified by conversion into its various salts. The *aurichloride* does not melt sharply; the *platinichloride* begins to decompose at 250°; the *mercurichloride* melts at 185°, whilst the *picrate* melts and decomposes at 194°.

4-*Allylpyridine mercurichloride*, prepared from the product obtained by interaction of 4-methylpyridine and paraldehyde, crystallises in needles and melts at 150°. The *hydrochloride* forms transparent crystals and melts and decomposes at 247°. The *base* is a colourless liquid and boils at 200—202°; its *platinichloride* melts and decomposes at 206°; its *aurichloride* melts and decomposes at 174°, whilst its *picrate* melts and decomposes at 169—170°.

4-Allylpyridine was reduced by sodium ethoxide, the reduction product converted into its nitroso-derivative, from which 4-coniine hydrochloride was prepared. 4-*Coniine* is a colourless liquid and boils at 178—180°. Its *platinichloride* and *hydrochloride* were analysed.

A. McK.

4-Stilbazole. CONRAD FRIEDLÄNDER (*Ber.*, 1905, **38**, 159—160. Compare preceding abstract).—4-*Stilbazole*, prepared by the condensation of 4-methylpyridine and benzaldehyde, separates from alcohol in glistening leaflets and melts at 127°. Its *hydrochloride* forms yellowish-green needles and melts at 204°; the *hydrobromide* forms brownish-red needles and melts at 174°; the *picrate* melts at 213°; the *hydrogen tartrate* melts at 164—165°; the *zincochloride* forms

yellow needles, which soften at about 230° and melt at 250°; the *aurichloride* forms red needles and melts at 205°; the *platinichloride* melts at 310°; the *bromine additive compound*, $C_{13}H_{11}NBr_2$, melts indefinitely at 228—230°. A. McK.

4-Pyrophthalone. Erich Düring (*Ber.*, 1905, **38**, 161—164. Compare preceding abstracts; Eibner, Abstr., 1901, i, 348, 611; Huber, Abstr., 1903, i, 576).—4-*Pyrophthalone*,

$$CO{<}^{\text{—O—}}_{C_6H_4}{>}C{:}CH{\cdot}C_5NH_4,$$

prepared by the condensation of 4-methylpyridine and phthalic anhydride by zinc chloride, separates from a mixture of ethyl alcohol and glacial acetic acid in glistening, orange-coloured needles, which begin to decompose at 250°. The *hydrochloride* forms red needles; the *mercuric chloride double salt* forms orange-red needles which decompose at about 271°; the *platinichloride* begins to decompose at 260°. The *sodium* salt is crimson.

Stilbazyl alcohol, $OH{\cdot}CH_2{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}C_5NH_4$, prepared by the reduction of 4-pyrophthalone in glacial acetic acid solution by zinc dust, forms the *hydrochloride*, which is bright yellow and begins to decompose at 210°; the *hydrobromide* decomposes at 230°; the *nitrate* melts at 160—165°; the *aurichloride* decomposes at 165—167°; the *platinichloride* melts and decomposes at 185°.

Tetrachloro-4-pyrophthalone, $CO{<}^{\text{—O—}}_{C_6Cl_4}{>}C{:}CH{\cdot}C_5NH_4$, prepared from 4-methylpyridine and tetrachlorophthalic anhydride, forms a dark green powder. A. McK.

Reduction Products of 4′-Methyl-4-stilbazole. 4-ω-Trichlorohydroxypropylpyridine. Erich Düring (*Ber.*, 1905, **38**, 164—167. Compare preceding abstracts).—4′-*Methyl-4-stilbazole*, $C_6H_4Me{\cdot}CH{:}CH{\cdot}C_5NH_4$, prepared by the condensation of 4-methylpyridine with *p*-tolualdehyde, separates from alcohol in white crystals, which soften at 80° and melt at 101—102°. Its *hydrochloride* melts at 120°; its *hydrobromide* melts at 176—177°; its *mercurichloride* softens at 195° and begins to melt at 208°; its *aurichloride* melts and decomposes at 191°; its *platinichloride* melts and decomposes at 193°.

When reduced by hydriodic acid and red phosphorus, 4′-methyl-4-stilbazole forms 4′-*methyldihydro-4-stilbazole*, $C_6H_4Me{\cdot}CH_2{\cdot}CH_2{\cdot}C_5NH_4$, a colourless liquid which boils at 220° under 80 mm. pressure; the *hydrochloride* softens at 135° and begins to melt at 140°; the *hydrobromide* melts at 149—150°; the *hydriodide* softens at 132° and melts at 138°; the *mercurichloride* melts indefinitely at 110°; the *aurichloride* melts at 155°; the *platinichloride* melts and decomposes at 194°.

4′-*Methyl-4-stilbazoline*, $C_6H_4Me{\cdot}CH_2{\cdot}CH_2{\cdot}C_5NH_{10}$, prepared by the reduction of 4′-methyl-4-stilbazole by sodium ethoxide, is a colourless liquid which boils at 215°; its *platinichloride* melts and decomposes at 205°.

4-ω-*Trichloro-β-hydroxypropylpyridine*, $CCl_3{\cdot}CH(OH){\cdot}CH_2{\cdot}C_5NH_4$,

prepared from 4-methylpyridine and chloral, forms glistening plates and melts at 160°; its *platinichloride* melts and decomposes at 198°.

A. McK.

Pyridine-2 : 3 : 4-tricarboxylic Acid. ALFRED KIRPAL (*Monatsh.*, 1905, 26, 53—64).—The *anhydride* of pyridine-2 : 3 : 4-tricarboxylic acid is formed when the tricarboxylic acid is warmed with acetic anhydride at 30—40°; it melts at 170°, and when heated on the water-bath with acetic anhydride yields cinchomeronic anhydride, which is also formed when the tricarboxylic acid is boiled with acetic anhydride The tricarboxylic anhydride is therefore to be represented by the formula $\begin{array}{l}\mathrm{CH{:}CH{-\!\!-\!\!-}C{\cdot}CO} \\ \mathrm{N{=}C(CO_2H){\cdot}C{\cdot}CO}\end{array}\!\!>\!O$, and Meyer's anhydride chloride (Abstr., 1901, i, 750) by $\begin{array}{l}\mathrm{CH{:}CH{-\!\!-\!\!-}C{\cdot}CO} \\ \mathrm{N{=}C(COCl){\cdot}C{\cdot}CO}\end{array}\!\!>\!O$. The 3-*methyl* ester, $\begin{array}{l}\mathrm{CH{:}CH{-\!\!-\!\!-}C{\cdot}CO_2H} \\ \mathrm{N{=}C(CO_2H){\cdot}C{\cdot}CO_2Me}\end{array}$ (compare Wegscheider, Abstr., 1902, i, 618), is formed by warming the anhydride with methyl alcohol; it crystallises in glistening plates, melts at 170°, and when heated with methyl-alcoholic hydrogen chloride yields the trimethyl ester, which melts at 102° (m. p. 97°, Meyer, *loc. cit.*). The action of aqueous ammonia on the 3-methyl ester leads to the formation of the *ammonium* salt of the monamic acid, $NH_2{\cdot}CO{\cdot}C_5NH_2(CO_2NH_4)_2$, which crystallises in colourless, flat needles, loses $1H_2O$ at 100°, and melts and decomposes at 150°. The *amic* acid, $C_8H_6O_5N_2$, crystallises in colourless prisms, melts at 180°, and when heated above its melting point yields cinchomeronimine. The dimethyl ester melts at 183° (Rint, Abstr., 1897, i, 485, gives m. p. 166°) and yields traces of the trimethyl ester on prolonged boiling with methyl-alcoholic hydrochloric acid, in agreement with the constitution

$$N\!<\!\begin{array}{l}\mathrm{CH{\cdot}C(CO_2Me)} \\ \mathrm{CH{:}C(CO_2Me)}\end{array}\!\!>\!C{\cdot}CO_2H.$$

Contrary to expectation, the diethyl ester of pyridine-2 : 3 : 4-tricarboxylic acid yields diethyl cinchomeronate when heated at 150—160° or with alcoholic hydrochloric acid under pressure, which points to the constitution $N\!<\!\begin{array}{l}\mathrm{CH{\cdot}C(CO_2Et)} \\ \mathrm{CH{:}C(CO_2H)}\end{array}\!\!>\!C{\cdot}CO_2Et$. When warmed in a reflux apparatus with methyl iodide and aqueous sodium carbonate, pyridine-2 : 3 : 4-tricarboxylic acid yields the *betaine*,

$$\mathrm{CH}\!\begin{array}{l}\nearrow\mathrm{C(CO_2H){\cdot}C}\searrow\!{-\!\!-\!\!-\!\!-\!\!-}\mathrm{CO} \\ \qquad\qquad\qquad\quad\mathrm{C{\cdot}CO_2H}\ | \ (?), \\ \searrow\mathrm{CH{=}NMe}\nearrow\!{-\!\!-\!\!-\!\!-\!\!-}\mathrm{O}\end{array}$$

which crystallises in small, colourless prisms, becomes brown at 180°, melts and decomposes at 220°, and when boiled with water yields apophyllenic acid.

G. Y.

Action of Allyl Iodide on Tetrahydroquinoline. EDGAR WEDEKIND (*Ber.*, 1905, 38, 436—440).—The compound described by Wedekind and Oechslen (Abstr., 1903, i, 116) as 1-allyltetrahydroquinoline hydriodide does not contain allyl, and is really tetrahydroquinoline hydriodide, being formed by the following reaction:

$$C_9H_{10}N{\cdot}C_3H_5 + C_2H_5I = C_9H_{10}{:}NH_2I + C_3H_6 + C_2H_2,$$

the allyl group being expelled from the tertiary base by the action of ethyl iodide. The reaction between allyl iodide and tetrahydroquinoline proceeds differently in the presence or absence of alcohol; in the first case, addition taking place to form 1-allyltetrahydroquinoline hydriodide, and in the second hydrogen iodide being formed, which combines with unaltered tetrahydroquinoline to form the hydriodide, allyltetrahydroquinoline remaining as the free base.

A repetition of the reaction between ethylene iodide and ethyl tetrahydro*iso*quinolino-2-acetate (Wedekind, Abstr., 1904, i, 96) has shown that the principal product is the hydriodide of the ester, $C_{28}H_{38}O_4N_2I_2$, melting at 153—154°. It was not found possible to obtain again the iodide melting at 168—169°. C. H. D.

7-Aminoquinaldine [7-Amino-2-methylquinoline]. E. ALBER (*J. pr. Chem.*, 1905, [ii], **71**, 39—54. Compare Doebner and Miller, Abstr., 1884, 1373; Gerdeisen, Abstr., 1889, 520).—The action of nitric acid of sp. gr. 1·49 on benzylacetone at −18° leads to the formation of a mixture of *p*- and *o*-nitrobenzylacetones. p-*Nitrobenzylacetone*, $NO_2\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot COMe$, crystallises in long, white needles, melts at 42°, boils at 204° under 13 mm. pressure, and is identical with Wortsmann's product (*Inaug. Diss.*, Basel, 1903), obtained by hydrolysis of ethyl *p*-nitrobenzylacetonedicarboxylate. The *phenylhydrazone* of *p*-nitrobenzylacetone forms yellow crystals, melts at 103°, and decomposes on exposure to light, more slowly in the dark.

op-*Dinitrobenzylacetone* is formed by the action of nitric acid of sp. gr. 1·52 on the mononitro-compounds in concentrated sulphuric acid, or on benzylacetone in fuming sulphuric acid at −18°. It crystallises in small, colourless, rhombic leaflets, in long prisms, or in large plates, melts at 58—59°, and, when warmed with aqueous potassium hydroxide, forms a dark red solution.

A reduction of the dinitro-compound with stannous chloride and concentrated hydrochloric acid leads to the formation of 7-*amino*-2-*methylquinoline*, which crystallises in long, slender, colourless needles, melts at 148°, is easily volatile in a current of steam, forms a violet-blue fluorescent solution in ether, which shows a green fluorescence when poured into water, and when diazotised and "coupled" with β-naphthol in alkaline solution forms a dark red dye. The *hydrochloride* crystallises in microscopic, yellow needles and dissolves in water to a solution with intensely green fluorescence; the *tin double* salt crystallises in leaflets and dyes tannated cotton-wool yellow; these salts give the pine-wood pyrrole reaction. The *benzoyl* derivative, $C_{17}H_{14}ON_2,H_2O$, crystallises in small, white needles, loses H_2O at 100°, melts at 172—173°, and forms a fluorescent blue solution in dilute hydrochloric acid. The *acetyl* derivative, $C_{12}H_{12}ON_2$, crystallises in long, yellow needles, melts at 192°, is easily soluble in alcohol, but only slightly so in benzene or petroleum, dissolves in dilute acids to blue fluorescent solutions, and gives the pine-wood reaction. The *picrate*, $C_{10}H_{10}N_2,C_6H_3O_7N_3$, crystallises in long, yellow needles and melts at 213—214°.

The properties described show the author's 7-amino-2-methyl-

quinoline to be isomeric, and not identical, with Doebner and Miller's base (*loc. cit.*), obtained by reduction of 7-nitro-2-methylquinoline.

G. Y.

α-Naphthoyltetrahydroquinoline. JULIUS VON BRAUN (*Ber.*, 1905, **38**, 179—181).—α-Naphthoyl chloride, prepared by the action of phosphorus pentachloride on α-naphthoic acid, is a transparent liquid and boils at 172—173° under 15 mm. pressure. 1-α-*Naphthoyltetrahydroquinoline*, $C_6H_4<\begin{matrix}N(CO\cdot C_{10}H_7)\\CH_2\text{——}CH_2\end{matrix}>CH_2$, prepared by shaking α-naphthoyl chloride with an alkali hydroxide and tetrahydroquinoline, forms colourless crystals and melts at 115°. When the amide is gradually heated at 160° with phosphorus pentachloride, the acid chloride,

$$C_{10}H_7\cdot CCl\colon N\cdot C_6H_4\cdot C_3H_6Cl,$$

first formed, is transformed into *naphthoyl-o-γ-chloropropylanilide*,

$$C_{10}H_7\cdot CO\cdot NH\cdot C_6H_4\cdot C_3H_6Cl,$$

which forms red crystals and melts at 133°. A. McK.

Constitution of α-Naphthindole. ROBERT PSCHORR and E. KUHTZ (*Ber.*, 1905, **38**, 217—219).—α-Naphthindole is easily prepared, in a manner analogous to Hinsberg's preparation of β-naphthindole (Abstr., 1888, 372), by distillation of α-naphthoxindole with zinc dust, and is identical with Schlieper's naphthindole (Abstr., 1887, 153, 963). To settle whether the nitrogen ring is attached to the naphthalene ring at the 1 : 2 or 1 : 8 position, an attempt was made to condense 1-amino-2-ethoxynaphthalene and 1-aminonaphthalene-8-sulphonic acid (in which the 2 and 8 positions respectively are already occupied) with glyoxal sodium bisulphite by Hinsberg's method. Only in the latter compound, substituted in the 8 position, was a naphthindole derivative, *α-naphthindoledisulphonic acid*, obtained, which, on heating with zinc dust, was converted into naphthindole ; this therefore has the constitution

$$\begin{matrix}C_6H_4\text{——}C\cdot NH\\ | \qquad\qquad \| \\ CH\colon CH\cdot C\cdot CH\end{matrix}>CH.$$

E. F. A.

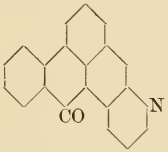
2 : 2-Dinaphtha-1 : 1-imine [αα-Di-β-naphthacarbazole]. VICTOR VESELY (*Ber.*, 1905, **38**, 136—139. Compare Nietzki and Goll, Abstr., 1886, 245 ; Meissenheimer and Witte, Abstr., 1904, i, 193).—2-*Chloro*-1-*nitronaphthalene*, $C_{10}H_6O_2NCl$, prepared from 1-nitro-β-naphthylamine by Votóček and Zeníšek's method (Abstr., 1900, i, 19), crystallises in yellow needles, melts at 95·5°, distils without decomposition above 360°, and is reduced by zinc dust in glacial acetic acid solution to 2-chloro-α-naphthylamine (Cleve, Abstr., 1887, 961). 2-Bromo-1-nitronaphthalene, obtained in the same manner, crystallises in slender, yellow needles, melts at 102—103°, and distils, without decomposition, above 360°.

When boiled with copper powder in nitrobenzene solution, 2-iodo-1-nitronaphthalene (Meldola, Trans., 1885, **47**, 521) yields 1 : 1-*dinitro*-2 : 2-*dinaphthyl*, $C_{20}H_{12}O_4N_2$, which crystallises in colourless scales, commences to blacken at 265°, melts at 276°, and is reduced by zinc dust, in glacial acetic acid solution, to 2 : 2-dinaphtha-1 : 1-imine,

$$CH<\begin{matrix}C_6H_4\cdot C\cdot NH\cdot C\cdot C_6H_4\\ \qquad\ \ \| \qquad\quad \| \\ CH\text{—}C\text{———}C\text{—}CH\end{matrix}>CH.$$

This is identical with Nietzki and Goll's dinaphthacarbazole (*loc. cit.*). The constitution of the two bases obtained by these authors from 1 : 1-hydrazonaphthalene must be $C_6H_4<\begin{matrix}C(NH_2):C—C:C(NH_2)\\ CH=\!=\!=CH\ \ CH=CH\end{matrix}>C_6H_4$ for dinaphthyline, and $NH_2\cdot C\lessgtr\begin{matrix}-C_6H_4-\\ CH\cdot CH\end{matrix}\gtrless C\cdot C\lessgtr\begin{matrix}-C_6H_4-\\ CH\cdot CH\end{matrix}\gtrless C\cdot NH_2$ for naphthidine. G. Y.

Syntheses in the Anthracene Series and New Dyes. Oscar Bally (*Ber.*, 1905, **38**, 194—196).—When β-aminoanthraquinone is condensed with glycerol as in the ordinary Skraup's synthesis, the product is not Graebe's anthraquinolinequinone (*Annalen*, 1880, **201**, 349), but *benzanthronequinoline*, $C_{20}H_{11}ON$, which crystallises from toluene in needles melting at 251°. The same compound is also formed when anthraquinonequinoline is condensed with glycerol, and is represented by the formula



Anthranol or anthraquinone readily condenses with glycerol, yielding *benzanthrone* itself, $C_{17}H_{10}O$, which melts at 170°. Compounds of this type, when fused with alkali, yield dyes. J. J. S.

Azlactones [Alkylideneoxazolones] and their Transformations. Emil Erlenmeyer, jun. (*Annalen*, 1904, **337**, 265—271. Compare Abstr., 1902, i, 595 ; this vol., i, 131).—Although α-amino-acids and their mono-alkyl derivatives readily yield dimolecular anhydrides, hippuric acid is not capable of such a reaction, but its alkylidene derivatives, $R\cdot CH:C(NHBz)\cdot CO_2H$, on the other hand, give internal anhydrides. Since these anhydrides are converted by ammonia into amides, $R\cdot CH:C(NHBz)\cdot CO\cdot NH_2$, which lose water and yield compounds possessing the characters of acid imides, and having the probable formula $CHPh:C<\begin{matrix}N=CPh\\ CO\cdot NH\end{matrix}$, it seems likely that the anhydrides are formed from the tautomeric hippuric acids,

$$R\cdot CH:C[NPh:C(OH)]\cdot CO\cdot NH_2,$$

and consequently are represented by the formula

$$CHPh:C<\begin{matrix}N=CPh\\ CO\cdot O\end{matrix}.$$

The name "azlactone" [alkylideneoxazolone] is given to such anhydrides of the general form $R\cdot CH:C<\begin{matrix}N=CR\\ CO\cdot O\end{matrix}$, a formula which accounts for their formation from α-acylamino-acids only and their yellow colour. The latter depends not only on the ring, but also on the nature and position of the substituting groups. K. J. P. O.

Azlactones [Alkylideneoxazolones] from Cinnamaldehyde or Cuminaldehyde and Hippuric Acid. EMIL ERLENMEYER, jun., and O. MATTER (*Annalen*, 1904, **337**, 271—282. Compare preceding abstract).—On heating cinnamaldehyde, hippuric acid, and sodium acetate with acetic anhydride at 100°, the *azlactone* [2-*phenyl*-4-*cinnamylideneoxazolone*], $CHPh:CH\cdot CH:C<\begin{matrix}N=CPh\\ CO\cdot O\end{matrix}$, is obtained as orange-yellow needles melting at 152°, which can only be purified by conversion into cinnamylidenehippuric acid, $CHPh:CH\cdot CH:C(NHBz)\cdot CO_2H$, by warming with aqueous sodium hydroxide; it crystallises in yellow needles, melting and decomposing at 238°, and is reconverted into the azlactone by heating with acetic anhydride. After prolonged heating with hydrochloric acid under pressure at 120°, the acid is decomposed into carbon dioxide, benzoic acid, naphthalene, and α-naphthoic acid. The intermediate unsaturated ketonic acid, $CHPh:CH\cdot CH_2\cdot CO\cdot CO_2H$, could not be isolated. The *ethyl* ester of cinnamylidenehippuric acid, prepared by dissolving the acid in alcoholic sodium hydroxide, crystallises in colourless needles melting at 132°.

Cuminaldehyde and hippuric acid yield the *azlactone* [2-*phenyl*-4-*cumylideneoxazolone*], $C_6H_4Pr^{\beta}\cdot CH:C<\begin{matrix}N=CPh\\ CO\cdot O\end{matrix}$, which crystallises in yellow needles melting at 121°. *Cumylidenehippuric acid*,
$C_6H_4Pr^{\beta}\cdot CH:C(NHBz)\cdot CO_2H$,
is obtained as colourless needles melting at 201° by dissolving the azlactone in sodium hydroxide; the *methyl* ester forms crystals melting at 128°, and the *ethyl* ester colourless needles melting at 164°. The *amide* prepared by treating the azlactone with ammonia crystallises in colourless needles melting at 170°. When warmed with sodium hydroxide, it yields the *imide*, $C_6H_4Pr^{\beta}\cdot CH:C<\begin{matrix}N=CPh\\ CO\cdot O\end{matrix}$, which crystallises in yellow needles melting at 245°. If the azlactone is boiled for 3 to 4 hours with sodium hydroxide (3 mols.), the *sodium* salt of p-iso*propylphenylpyruvic acid*, $C_6H_4Pr^{\beta}\cdot CH_2\cdot CO\cdot CO_2H$, is obtained; the free *acid* crystallises in leaflets melting at 78°, decomposes in the air, and gives a green coloration with ferric chloride. The keto-acid condenses with benzaldehyde in the presence of concentrated hydrochloric acid, yielding the *oxylactone*, $C_6H_4Pr^{\beta}\cdot CH<\begin{matrix}CHPh\cdot O\\ CO——CO\end{matrix}$, which crystallises in colourless leaflets, melting at 212°, and giving a green coloration with ferric chloride. K. J. P. O.

Azlactones [Alkylideneoxazolones] from Furfuraldehyde, or Salicylaldehyde and Hippuric Acid. EMIL ERLENMEYER, jun., and WERNER STADLIN (*Annalen*, 1904, **337**, 283—293. Compare preceding abstracts).—Furfuraldehyde and hippuric acid yield the *azlactone* [2-*phenyl*-4-*furfurylideneoxazolone*], $C_4OH_3\cdot CH:C<\begin{matrix}N=CPh\\ CO\cdot O\end{matrix}$, which crystallises in golden-yellow needles melting at 171°; by warming with dilute sodium hydroxide, it is converted into *furfurylidene-*

hippuric acid, $C_4OH_3 \cdot CH\colon C(NHBz) \cdot CO_2H$; the latter crystallises in leaflets melting at 210°. The *methyl* ester is formed when the azlactone is warmed with a methyl-alcoholic solution of potassium hydroxide and crystallises in leaflets melting at 141°, and the *ethyl* ester in colourless needles melting at 132—133°. The *amide* is prepared by the action of ammonia on the azlactone, and forms pale yellow needles melting at 184°. The *imide*, $C_4OH_3 \cdot CH\colon C<\begin{matrix} N=CPh \\ CO \cdot NH \end{matrix}$, prepared by warming the amide with sodium hydroxide solution, is an intensely yellow, insoluble substance decomposing at 241°. The *piperidide*, $C_4OH_3 \cdot CH\colon C(NHBz) \cdot CO \cdot C_5NH_{10}$, is obtained by warming the azlactone with alcoholic piperidine solution, as colourless needles melting at 162—163°.

The interaction of salicylaldehyde and hippuric acid has been previously studied by Plöchl, Wolfrum, and Rebuffat (*Ber.*, 1885, **18**, 1183), who isolated two substances, one a yellow substance, $C_{32}H_{24}O_7N_2$ or $C_{16}H_{13}O_4N$, which is now shown to be the *azlactone* [2-*phenyl*-4-o-*acetoxybenzylideneoxazolone*],

$$OAc \cdot C_6H_4 \cdot CH\colon C<\begin{matrix} N=CPh \\ CO \cdot O \end{matrix};$$

the other substance is the colourless *benzoylaminocoumarin*,

$$C_6H_4<\begin{matrix} O - CO \\ CH\colon C \cdot NHBz \end{matrix},$$

which was thought to be benzoyliminocoumarin. These two substances are formed from the normal primary product, *benzoylaminocoumaric acid*, $OH \cdot C_6H_4 \cdot CH\colon C(NHBz) \cdot CO_2H$, which then loses water in two different ways, possibly from the two stereoisomeric forms. The substance which is formed from the coumarone by the action of sodium hydroxide is not salicylglycidic acid, but o-*hydroxyphenylpyruvic acid*, which immediately condenses to oxycoumarin, $C_6H_4<\begin{matrix} O - CO \\ CH_2 \cdot CO \end{matrix}$.

The azlactone is prepared by heating hippuric acid, salicylaldehyde, and sodium acetate with acetic anhydride on the water-bath, and is contained in the first alcoholic extracts of the product, whilst the benzoylaminocoumarin is found in the last extracts; it crystallises in pale yellow leaflets melting at 137—138°, and is converted by heating with 10 per cent. sodium hydroxide into benzoylaminocoumarin and benzoylaminocoumaric acid,

$$OH \cdot C_6H_4 \cdot CH\colon C(NHBz) \cdot CO_2H;$$

the latter forms colourless crystals melting at 185°. Benzoylaminocoumarin crystallises in needles melting at 172—173°, and is insoluble in sodium carbonate solution. When either the azlactone or benzoylaminocoumarin is boiled with sodium hydroxide, the oxycoumarin is obtained as needles melting at 152°, which give a green coloration with ferric chloride. It yields a *phenylhydrazone*, $C_{15}H_{12}O_2N_2$, which crystallises in yellow plates melting at 173—174°, and also condenses with *o*-phenylenediamine giving the *compound* $C_{15}H_{10}ON_2$, which crystallises in colourless needles melting at 230°. The azlactone could not be converted into an ester.

Attempts to obtain isomerides of tyrosine from benzoylamino-coumaric acid were not successful. K. J. P. O.

Azlactones [Alkylideneoxazolones] formed in the Condensation of *m*-Hydroxybenzaldehyde or Anisaldehyde with Hippuric Acid. Emil Erlenmeyer, jun., and Fritz Wittenberg (*Annalen*, 1904, **337**, 294—301. Compare preceding abstracts).—The *acetylazlactone* [*2-phenyl-4-*m*-acetoxybenzylideneoxazolone*],

$$OAc\cdot C_6H_4\cdot CH\colon C<\begin{matrix}N=CPh\\ CO\cdot O\end{matrix},$$

is prepared from *m*-hydroxybenzaldehyde and hippuric acid, and forms crystals melting at 145°; when treated with sodium hydroxide, the m-*hydroxybenzylidenehippuric acid*, $OH\cdot C_6H_4\cdot CH\colon C(NHBz)\cdot CO_2H$, is obtained as crystals melting at 204°; the *ethyl* ester crystallises in needles melting at 118°; the *piperidide*, which is prepared by heating the azlactone with alcoholic piperidine, crystallises in colourless needles melting at 201°.

The corresponding p-*methoxy*-compound,

$$OMe\cdot C_6H_4\cdot CH\colon C<\begin{matrix}N=CPh\\ CO\cdot O\end{matrix},$$

is prepared from anisaldehyde and hippuric acid, and crystallises in yellow needles melting at 156·5°; when warmed with sodium hydroxide, p-*methoxybenzylidenehippuric acid*, $OMe\cdot C_6H_4\cdot CH\colon C(NHBz)\cdot CO_2H$, is formed as colourless needles melting and decomposing at 225°; the *methyl* ester, prepared from the azlactone and methyl alcoholic sodium hydroxide, forms colourless leaflets melting at 153°, and the *amide*, prepared from the azlactone and ammonia, colourless crystals melting at 187°. The *imide*, $OMe\cdot C_6H_4\cdot CH\colon C<\begin{matrix}N=CPh\\ CO\cdot NH\end{matrix}$, prepared from the amide by the action of sodium hydroxide, crystallises in yellow needles melting at 283°. The *piperidide*,

$$OMe\cdot C_6H_4\cdot CH\colon C(NHBz)\cdot CO\cdot C_5NH_{10},$$

prepared from the azlactone and alcoholic piperidine, crystallises in colourless leaflets melting at 173°. p-*Methoxyphenylpyruvic acid*, $OMe\cdot C_6H_4\cdot CH_2\cdot CO\cdot CO_2H$, is obtained by boiling the azlactone for several hours with a slight excess of 10 per cent. sodium hydroxide, and crystallises in prisms melting at 186°; it gives a green coloration with ferric chloride and decomposes on keeping. Its *phenylhydrazone*, $C_{16}H_{16}O_3N_2$, crystallises in colourless leaflets melting at 154°. In the presence of concentrated hydrochloric acid, the keto-acid condenses with benzaldehyde, forming the *a-oxylactone*,

$$OMe\cdot C_6H_4\cdot CH<\begin{matrix}CHPh\cdot O\\ CO\text{———}CO\end{matrix},$$

which crystallises in prisms with 1 mol. of alcohol, melting at 180°.
K. J. P. O.

Condensation of Pyruvic Acid with Hippuric Acid. Emil Erlenmeyer, jun., and E. Arbenz (*Annalen*, 1904, **337**, 302—306. Compare preceding abstracts).—The condensation of pyruvic acid with hippuric acid was first investigated by Hoffmann (*Ber.*, 1886, **19**,

2555), who obtained a compound which is now shown to be the carboxylic acid, $CO_2H\cdot CMe:C<\begin{matrix}N{=}CPh\\ CO\cdot O\end{matrix}$; it forms colourless crystals melting at 157°. By alkali hydroxides, the acid,

$$CO_2H\cdot CMe:C(NHBz)\cdot CO_2H,$$

is probably formed, but on setting it free from its salts is immediately reconverted into the azlactone. When the azlactone is boiled with barium carbonate, the *barium* salt, $C_{12}H_9O_5NBa,2HO$, is formed.

When treated with dilute sulphuric acid, the azlactone undergoes the characteristic decomposition, ammonia, benzoic acid, and methyl-oxalacetic acid being produced; the latter, however, decomposes into carbon dioxide and methylpyruvic acid, which was identified by means of a characteristic barium salt, and its phenylhydrazone, and in addition by its conversion into scatolecarboxylic acid and scatole.

K. J. P. O.

Methylation of Dibenzenesulphonebenzidine. OSCAR HINSBERG (*Ber.*, 1905, **38**, 554. Compare Abstr., 1893, i, 168; Willstätter and Kalb, Abstr., 1904, i, 1050).—Dibenzenesulphonedimethylbenzidine, prepared by heating dibenzenesulphonebenzidine with methyl iodide, methyl alcohol, and aqueous sodium hydroxide under pressure at 100°, melts at 189—190°. When the reaction takes place in an open vessel, the methylation is not complete; the melting point 179—180°, previously observed, was that of a mixture so obtained.

G. Y.

Action of Secondary Aromatic Amines on Dinitrophenylpyridinium Chloride. THEODOR ZINCKE and W. WÜRKER (*Annalen*, 1905, **338**, 107—141).—It has been shown that primary aromatic bases such as aniline interact with dinitropyridinium chloride, yielding, besides dinitroaniline, a red salt of a univalent base, for which either the formula $NPh:CH\cdot CH:CH\cdot CH:CH\cdot NHPh$ or

$$CH<\begin{matrix}CH\cdot NPh\\ CH{=}CH\end{matrix}>CH\cdot NHPh$$

was suggested. König imagines that the substance is desmotropic, and can be represented by either formula. Similar compounds have now been obtained by the action of methylaniline on the pyridinium chloride, which is decomposed by alkali hydroxides, giving the aldehyde, $NMePh\cdot CH:CH\cdot CH:CH\cdot CHO$, and methylaniline. The original salt must therefore have the formula

$$NMePh\cdot CH:CH\cdot CH:CH\cdot CH:NMePhCl.$$

The methylaniline group can easily be replaced by an oxime or hydrazone group, or by aniline or *p*-chloroaniline. These reactions are all in favour of the open chain formula.

Dinitrophenylpyridinium chloride is heated in alcoholic solution with methylaniline and the product poured into dilute hydrochloric acid; the compound $NMePh\cdot CH:CH\cdot CH:CH\cdot CH:NMePhCl$ crystallises with $1\frac{1}{2}H_2O$ from water and with HCl and 3MeOH from methyl-alcoholic hydrochloric acid, and melts and decomposes at 116—118°; it forms a colourless solution in concentrated sulphuric acid, but yields a red sulphate. Its acetic acid solution gives a brownish-red

precipitate with potassium dichromate, and its alcoholic solution with potassium tri-iodide a *periodide*, which crystallises in violet needles melting and decomposing at 170—172°.

Methyl-*p*-bromoaniline (which is a yellow oil boiling at 136—138° under 12 mm. pressure) and the pyridinium salt react giving the *compound* $C_6H_4Br{\cdot}NMe{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH{:}NClMe{\cdot}C_6H_4Br$, which crystallises in red leaflets or needles, sintering at 200° and melting and decomposing at 205—208°; it dissolves without colour in concentrated sulphuric acid; on dilution, the *sulphate* is precipitated as red flocks. The *platinichloride*, $(C_{19}H_{19}Br_2N_2)_2PtCl_6$, is a brick-red, crystalline powder sintering at 170°, melting and decomposing at 187°.

When the methylaniline compound is boiled with 20 per cent. methylalcoholic sodium carbonate solution and the product acidified with acetic acid, the *compound* $NMePh{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CHO$ is obtained as yellow needles melting and decomposing at 78—80°; it is soluble in dilute acids, but rapidly decomposed by them with the formation of methylaniline; it reduces an ammoniacal silver solution. It yields an *oxime* and a *phenylhydrazone*, which are also formed directly from the original methylaniline compound. It reacts with primary and secondary arylamines, and with methylaniline regenerates the original material. It forms double salts and a crystalline *platinichloride*, $(C_{12}H_{14}ON)_2PtCl_6$, which is a reddish-brown powder melting and decomposing at 157—160°. The *picrate* forms pale brown needles melting and decomposing at 142—144°.

The aldehyde, $C_6H_4Br{\cdot}NMe{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CHO$, obtained in a similar manner to the compound just described, crystallises in yellow plates or flattened needles melting and decomposing at 116—117°; its salts are unstable, and the *platinichloride*, $(C_{12}H_{13}ONBr)_2,PtCl_6$, is a pale brown, unstable powder. The *oxime* crystallises in pale yellow needles melting and decomposing at 115—117° and is insoluble in alkali hydroxides, but is dissolved and decomposed by acids; its solution in concentrated sulphuric acid has a blood-red coloration. The *phenylhydrazone* crystallises in pale yellow leaflets readily decomposed by acids.

The *compound* $NMePh{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH{:}NHPhCl$ is prepared by treating the aldehyde with aniline and hydrochloric acid, and crystallises in ruby-red needles melting and decomposing at 159—161°; the salt is converted into the *base* by alkalis. The *compound*

$$NMePh{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH{:}NHCl{\cdot}C_6H_4Cl$$

is prepared from the aldehyde and *p*-chloroaniline, and crystallises in red leaflets melting and decomposing at 115—118°; when boiled with hydrochloric acid, it is converted into *chlorophenylpyridinium chloride*. The free *base*, $C_{18}H_{17}N_2Cl$, is very stable and crystallises in needles which are dark brown by reflected and pale yellow by transmitted light; it melts and decomposes at 127°.

The aldehyde, $C_{12}H_{13}ON$, when treated with methyl-*p*-bromoaniline and hydrochloric acid, yields the *salt*,

$$NMePh{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH{:}NMeCl{\cdot}C_6H_4Br,$$

which forms a dark red, crystalline powder sintering and then melting and decomposing at 144°.

The *compound* $C_6H_4Br{\cdot}NMe{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH{:}NMePhCl$ is

formed from the aldehyde, $C_{12}H_{12}ONBr$, and methylaniline and is a purplish-red, crystalline powder melting and decomposing at 111—112°.

Cinnamaldehyde and methylaniline yield an unstable *compound*, CHPh:CH·CH:NMePhCl, which forms a *mercurichloride*, crystallising in orange-red needles, melting and decomposing at 167—169°, and a *platinichloride* which forms yellow crystals.

The methylaniline compound is decomposed by aniline and *p*-chloroaniline, both methylaniline groups being replaced by aniline groups. The *oxime*, NHPh·CH:CH·CH:CH·CH:NOH, and the *phenylhydrazone*, NHPh·CH:CH·CH:CH·CH:N_2HPh, of the dianilide which was previously described have now been prepared; the former crystallises in yellow needles melting and decomposing at 146°, and the latter in yellow leaflets melting and decomposing at 135°. K. J. P. O.

Malachite-green and Crystal-violet. RUDOLF LAMBRECHT and HUGO WEIL (*Ber.*, 1905, **38**, 270—282. Compare Abstr., 1904, i, 877).—*Tetramethyldiaminotriphenylcarbothiol*, SH·CPh:$(C_6H_4·NMe_2)_2$, obtained by passing hydrogen sulphide into a cold alcoholic solution of malachite-green containing acetic acid, crystallises from a mixture of benzene and alcohol as a colourless powder and melts at 153°; the analogous *compound*, SH·$C(C_6H_4·NMe_2)_3$, obtained from crystal-violet, melts at 159°. The same substances are obtained by using ammonium sulphide or sodium polysulphides instead of hydrogen sulphide. *Tetramethyldiaminothiobenzophenone*, $C_{17}H_{20}N_2S$, is obtained from the mother liquors of the carbothiol of crystal-violet, and crystallises from alcohol in steel-blue needles melting at 202°. The carbothiols are not decomposed when heated with benzene and sodium hydroxide or metallic sodium, but are reduced on boiling with alcohol through which hydrogen sulphide is passed to form leuco-malachite-green and leuco-crystal-violet.

When the carbothiol of malachite-green is heated with dilute acetic acid, it is rapidly decomposed, giving hydrogen sulphide and a solution of the quinonoid salt of the malachite-green base; on the other hand, an excess of dilute mineral acids under similar conditions only slowly eliminates hydrogen sulphide from the carbothiols, although the theoretical quantity of a dilute mineral acid brings about the loss of hydrogen sulphide at 50°.

The nature of the following salts illustrates the gradual production of colour from triphenylcarbinol bases.

Colourless Salts.—The *stannichloride* of *tetramethyldiaminotriphenylcarbothiol*, $C_{23}H_{26}N_2S,2HCl,SnCl_4,\frac{1}{2}H_2O$, is obtained by dissolving the carbothiol in ice-cold hydrochloric acid and adding stannic chloride. The analogous *derivative*, $C_{25}H_{31}N_3S,3HCl,1\frac{1}{2}SnCl_4,1\frac{1}{2}H_2O$, of crystal-violet is also colourless.

Orange-coloured Salts.—The *salt*

$$NMe_2Cl:C_6H_4:CPh·C_6H_4·NMe_2,HCl,SnCl_4,2\tfrac{1}{2}H_2O$$

is obtained in orange-red crystals by warming tetramethyldiaminotriphenylcarbinol with 30 per cent. hydrochloric acid and then adding stannic chloride. The analogous *salt*,

$$NMe_2Cl:C_6H_4:C:(C_6H_4·NMe_2,HCl)_2,2SnCl_4,2H_2O,$$

was obtained from the crystal-violet base.

Green Salts.—Under special conditions, the diacid *salt*,

$$NMe_2Cl{:}C_6H_4{:}C(C_6H_4{\cdot}NMe_2){\cdot}C_6H_4{\cdot}NMe_2,HCl,ZnCl_2,3H_2O,$$

derived from the crystal-violet base, can be obtained in bright green crystals; it corresponds with the ordinary green salt,

$$NMe_2Cl{:}C_6H_4{:}CPh{\cdot}C_6H_4{\cdot}NMe_2,$$

of the malachite-green base. W. A. D.

Replacement of the Hydroxyl Group by the Hydrazine Group. HARTWIG FRANZEN (*Ber.*, 1905, **38**, 266—270).—Two new methods of preparing hydrazines are described. α- or β-Naphthylhydrazine is formed on heating α- or β-naphthol, hydrazine sulphate, and hydrazine hydrate together with a little alcohol in a sealed tube for 8 hours at 100°. Hydrazine α- or β-hydroxynaphthoate, when heated at 140—150°, loses water and carbon dioxide, forming α- or β-naphthylhydrazine.

2 : 3-*Naphthylenedihydrazine*, $C_{10}H_6(NH{\cdot}NH_2)_2$, prepared from 2 : 3-dioxynaphthalene by the former method, crystallises in colourless, minute needles, melting and decomposing at 155—156°, which reduce Fehling's and ammoniacal silver solutions on warming; the *hydrochloride* forms a snow-white, crystalline mass without a sharp melting point. *Benzylidene*-2 : 3-*naphthylenedihydrazone*, $C_{10}H_6(NH{\cdot}N{:}CHPh)_2$, crystallises from benzene in yellow needles, which melt and decompose at 205°. 1 : 3-*Dibenzylideneamino*-2-*phenyl*-2 : 3-*naphthadihydroglyoxaline*, $C_{10}H_6{<}{\begin{matrix}N(N{:}CHPh)\\N(N{:}CHPh)\end{matrix}}{>}CHPh$, prepared by the interaction of the hydrazine with excess of benzaldehyde, crystallises from xylene in yellow needles melting and decomposing at 227—228°. E. F. A.

Nitroso- and Azo-derivatives of 3-Pyrazolones. AUGUST MICHAELIS (*Ber.*, 1905, **38**, 154—155).—Substitution in all three pyrazolones is readily effected in the 4-position. Halogen derivatives are formed by the action of chlorine or of bromine on solutions of 3-pyrazolones in glacial acetic acid or chloroform.

4-*Nitroso*-1-*phenyl*-5-*methyl*-3-*pyrazolone*, $NPh{<}{\begin{matrix}NH-CO\\CMe{:}\overset{|}{C}{\cdot}NO\end{matrix}}$, prepared by the action of sodium nitrite on a solution of 1-phenyl-5-methyl-3-pyrazolone in glacial acetic acid, separates from ethyl acetate in green needles and melts indefinitely at 159°.

The *azo*-compound, $NPh{<}{\begin{matrix}NH-CO\\CMe{:}\overset{|}{C}{\cdot}N{:}NPh\end{matrix}}$, formed by the action of diazobenzene chloride on an alkaline solution of 1-phenyl-5-methyl-3-pyrazolone, forms gold-coloured leaflets and melts at 99—100°. By the action of phosphorus oxychloride, it is converted into the 3-*chloropyrazole*, $NPh{<}{\begin{matrix}N{=\!=}CCl\\CMe{:}\overset{|}{C}{\cdot}N{:}NPh\end{matrix}}$. A. McK.

Amino-derivatives of Pyrimidine. SIEGMUND GABRIEL (*Ber.*, 1905, **38**, 149. Compare Abstr., 1902, i, 59; Traube, this vol., i, 101).—As Traube states 2 : 4 : 5 : 6-tetraminopyrimidine to be only a di-acid base, the author has repeated the preparation and analysis of

the hydrochloride and confirms his former statement that the composition is $C_4H_8N_6,3HCl$. G. Y.

Thio-derivatives of Pyrimidine. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 156055).—Thiocarbamide and its monoalkyl derivatives react with the sodium or potassium derivative of ethyl cyanoacetate to form pyrimidine compounds of the formula $NR<\begin{matrix}CO-CH_2\\C(SH):N\end{matrix}>C:NH$, which are readily converted into derivatives of hypoxanthine. The *compound* from ethyl cyanoacetate and thiocarbamide forms colourless crystals and dissolves readily in hot water and in dilute acids or alkalis. The preparation of compounds from methylthiocarbamide and allythiocarbamide is also described.

C. H. D.

Reduction of α-Dibenzylideneacetonehydroxylamineoxime. Gaetano Minunni and R. Ciusa (*Gazzetta*, 1904, **34**, ii, 373—376. Compare Minunni, Abstr., 1900, i, 237; Minunni and Carta-Satta, Abstr., 1900, i, 237).—Reduction of α-dibenzylideneacetonehydroxylamineoxime with sodium and amyl alcohol yields a *base*, $C_{17}H_{18}N_2$, which is either a pyrazoline derivative of the structure

$$CHPh:CH\cdot CH<\begin{matrix}CH_2\cdot CHPh\\NH-NH\end{matrix},$$

or a hydrazoethane compound having the formula

$$CHPh:CH\cdot CH<\begin{matrix}CH(CH_2Ph)\\NH\end{matrix}>NH.$$

The *hydrochloride* of the base is very hygroscopic; the *platinichloride*, $C_{17}H_{18}N_2,H_2PtCl_6$, forms a yellow, crystalline powder, readily soluble in water or alcohol. The *benzoyl* derivative, $C_{17}H_{17}N_2Bz$, crystallises from alcohol in white needles melting at 209—210°.

T. H. P.

Benziminazoles and their Decomposition. Otto Fischer (*Ber.*, 1905, **38**, 320—328. Compare Abstr., 1904, i, 195).—[With O. Veiel.]—1-Methylbenziminazole is best prepared by boiling methyl-*o*-phenylenediamine, obtained by reducing *o*-nitromethylaniline, with crystalline formic acid; it crystallises from light petroleum in white prisms, melts at 61°, and gives a *hydrochloride*, $C_8H_9N_2Cl$, crystallising from alcohol in needles; the *platinichloride*, $C_{16}H_{18}N_4PtCl_6,2H_2O$, forms reddish-yellow prisms and the *picrate* melts at 244°.

1 : 3-*Dibenzylbenziminazole hydrochloride*, $C_{21}H_{19}N_2Cl$, obtained by heating benziminazole with benzyl chloride for several hours at 100°, crystallises from alcohol; the *platinichloride* melts at 216°, the *aurichloride* at 155°, and the *picrate* at 208°. 1 : 3-*Dibenzylbenziminazole*-2-*ol*, $C_{21}H_{20}ON_2$, obtained by adding potassium hydroxide to a solution of the hydrochloride, crystallises from light petroleum in colourless nodules, melts at 113—114°, and when heated with concentrated alcoholic potassium hydroxide is resolved into formic acid and s-*dibenzyl*-o-*phenylenediamine*. The latter separates from light petroleum in thick crystals, melts at 71°, and gives a *hydrochloride*, $C_{20}H_{21}N_2Cl$, melting at 149°; it combines with salicylaldehyde to

form 2-o-*hydroxyphenyl*-1 : 3-*dibenzylhydrobenziminazole*, which crystallises from alcohol in white needles, melts at 136°, and is resolved by acids into its constituents. When *s*-dibenzyl-*o*-phenylenediamine is heated with acetic acid and a little acetic anhydride, 1 : 3-*dibenzyl*-2-*methylbenziminazole*-2-*ol*, $C_6H_4<\substack{N(C_7H_7)\\N(C_7H_7)}>CMe{\cdot}OH$, is obtained, crystallising from alcohol in white needles and melting at 153°; the *platinichloride*, $C_{44}H_{42}N_4PtCl_6$, forms yellow leaflets. On oxidation with ferric chloride in alcoholic solution, the diamine is converted into N-*tetrabenzyldiaminophenazonium chloride*, $C_{40}H_{36}N_4Cl_2,2H_2O$.

[With J. G. Mouson.]—5-*Bromobenziminazole*, $C_7H_5N_2Br$, prepared by heating 4-bromo-1 : 2-diaminobenzene with formic acid, crystallises from water in colourless needles, melts at 137°, and gives a crystalline *platinichloride* and *aurichloride*; when heated with an excess of methyl iodide, it is converted into 5-*bromo*-1 : 3-*dimethylbenziminazolium iodide* $C_9H_{10}N_2BrI$, which is easily decomposed by cold aqueous sodium hydroxide, giving 5-*bromo*-1 : 3-*dimethylbenziminazole*-2-*ol*,

$$C_9H_{11}ON_2Br;$$

the latter crystallises from light petroleum in white needles, melts at 103°, and is hydrolysed by boiling aqueous sodium hydroxide to 4-*bromo*-o-*phenylenedimethyldiamine*; this crystallises from dilute alcohol in needles and melts at 78°.

5-*Bromo*-1 : 2 : 3-*trimethylbenziminazolium iodide*, obtained by heating 5-bromo-2-methylbenziminazole with methyl iodide, crystallises from dilute alcohol in thick, yellow prisms and is with difficulty transformed by hot aqueous potassium hydroxide into 5-*bromo*-1 : 2 : 3-*trimethylbenziminazole*-2-*ol*, $C_6H_3Br<\substack{NMe\\NMe}>CMe{\cdot}OH$, which forms white needles and melts at 173°.

5-*Chloro*-1 : 2 : 3-*trimethylbenziminazolium iodide*, $C_{10}H_{12}N_2ClI$, prepared by the action of methyl iodide on 5-chloro-2-methylbenziminazole, is, however, converted into the corresponding *carbinol*,

$$C_{10}H_{13}ON_2Cl,$$

by gently warming it with aqueous sodium hydroxide; the product crystallises from alcohol in colourless prisms and melts at 152—153°.

W. A. D.

Synthesis of Derivatives of Ketoquinazoline. Bronislaw von Pawlewski (*Ber.*, 1905, **38**, 130—131).—4-*Keto*-2-*thion*-3-*phenyl*-1 : 2 : 3 : 4-*tetrahydroquinazoline*, $C_6H_4<\substack{CO-NPh\\NH{\cdot}CS}$, is formed when a molecular mixture of anthranilic acid and phenylthiocarbamide is heated at 160—165°. It crystallises from alcohol in small, irregular, nacreous leaflets, melts at 304—306°, and when treated with alkaline hydrogen peroxide solution is converted into 2 : 4-*diketo*-3-*phenyl*-1 : 2 : 3 : 4-*tetrahydroquinazoline*, $C_6H_4<\substack{CO-NPh\\NH{\cdot}CO}$, which is formed also when a molecular mixture of anthranilic acid and phenylcarbamide is heated at 160—180° and finally at 200°. It crystallises in long, colourless, flat prisms and needles, from glacial acetic acid in large

leaflets, melts at 275—277°, and dissolves in aqueous alkalis to solutions which, after dilution with water, have a violet fluorescence.

G. Y.

Quinoxaline and Benziminazole Compounds from 4-Nitro-2-aminodiphenylamine. ARNOLD REISSERT and G. GOLL (*Ber.*, 1905, **38**, 90—104).—4-Nitro-2-aminodiphenylamine (Nietzki and Almenräder, Abstr., 1896, i, 164) combines with potassium cyanide and formaldehyde in dilute alcoholic solution to form 5-*nitro*-2-*anilino-phenylglycine*, $NHPh\cdot C_6H_3(NO_2)\cdot NH\cdot CH_2\cdot CO_2H$, which melts at 96° after repeated precipitation from sodium carbonate solution by hydrochloric acid. It dissolves readily in alcohol, acetic acid, or acetone, sparingly in ether or benzene, but is partially dehydrated on heating, so cannot be recrystallised. On heating with concentrated sulphuric acid, water is removed and 6-*nitro*-2-*keto*-1-*phenyltetrahydroquinoxaline*, $NO_2\cdot C_6H_3{<}\begin{matrix}NH-CH_2\\ NPh\cdot CO\end{matrix}$, is formed; this crystallises from glacial acetic acid in bright yellow needles when slowly cooled, or in darker yellow tablets when rapidly cooled, and melts at 230·5° after drying at 100° in a vacuum. It dissolves in concentrated acids to colourless solutions, and is not decomposed on boiling. It is insoluble in benzene or ether, but dissolves readily in hot acetone. The same compound is obtained on heating nitroaminodiphenylamine with bromoacetic acid and sodium acetate.

Hydrogen chloride and stannous chloride reduce the acetic acid solution to 6-*amino*-2-*keto*-1-*phenyltetrahydroquinoxaline*, $C_{14}H_{13}ON_3$, which crystallises from alcohol in small, colourless needles melting at 158° and becoming yellow in the air. It is insoluble in alkalis, and dissolves readily in acetone or glacial acetic acid, very sparingly in ether or benzene. Ferric chloride oxidises the hydrochloride, an intense blue coloration, rapidly becoming brown, being produced.

The *diacetyl* derivative, $NHAc\cdot C_6H_3{<}\begin{matrix}NAc\cdot CH_2\\ NPh\cdot CO\end{matrix}$, crystallises from dilute acetic acid in star-shaped groups of colourless, lancet-like leaflets and melts at 128—131°.

Nitroaminodiphenylamine combines with ethyl oxalate (compare Meyer and Seeliger, Abstr., 1897, i, 45) on boiling to form 6-*nitro*-3-*hydroxy*-2-*keto*-1-*phenyldihydroquinoxaline*, $NO_2\cdot C_6H_3{<}\begin{matrix}N{=\!=}C\cdot OH\\ NPh\cdot CO\end{matrix}$, crystallising from ethyl oxalate or nitrobenzene in microscopic, colourless needles, remaining unaltered at 330°. Most organic solvents dissolve only traces. On boiling with a solution of sodium sulphide, 6-*amino*-3-*hydroxy*-2-*keto*-1-*phenyldihydroquinoxaline*, $C_{14}H_{11}O_2N_3$, is formed, and crystallises in slender, yellowish-white needles, not melting at 330°. It dissolves readily in acids or alkalis and is readily oxidised. The *sulphate* forms a colourless, sparingly soluble precipitate.

The *diacetyl* derivative, $NHAc\cdot C_6H_3{<}\begin{matrix}NAc\cdot CO\\ NPh\cdot CO\end{matrix}$,

$$NHAc\cdot C_6H_3{<}\begin{matrix}N{=\!=}C\cdot OAc\\ NPh\cdot CO\end{matrix}, \text{ or } NAc_2\cdot C_6H_3{<}\begin{matrix}N{=\!=}C\cdot OH\\ NPh\cdot CO\end{matrix},$$

forms small, colourless crystals, infusible at 300°, and dissolves readily in alkalis, thus suggesting the third of the above formulæ.

In the condensation of nitroaminodiphenylamine with ethyl oxalate, *ethyl* 5-*nitro*-1-*phenylbenziminazole*-2-*carboxylate*,

$$NO_2\cdot C_6H_3<\overset{N}{\underset{NPh}{}}>C\cdot CO_2Et,$$

is also produced, which crystallises from alcohol in colourless, tabular leaflets and melts at 150·5°. It dissolves readily in chloroform or hot acetic acid, acetone, or ethyl oxalate, sparingly in ether or benzene. The *carboxylic acid* forms a colourless, uncrystallisable powder, dissolving readily in alcohol, acetic acid, or acetone, sparingly in ether or benzene, and does not melt at 300°.

Concentrated hydrochloric acid decomposes the ester at 150°, forming 5-*nitro*-1-*phenylbenziminazole*, $NO_2\cdot C_6H_3<\overset{N}{\underset{NPh}{}}>CH$, which forms colourless crystals and melts at 159·5° and dissolves readily in acids. Stannous chloride reduces it to 5-*amino*-1-*phenylbenziminazole*, $C_{13}H_{11}N_3$, separating from benzene in colourless crystals and melting at 130—131°. The *stannochloride*, $C_{13}H_{11}N_3,2HCl,SnCl_2$, forms colourless needles. The *acetyl* derivative, $C_{15}H_{13}ON_3$, forms small, colourless crystals melting at 170·5° and yields a crystalline *hydrochloride*. C. H. D.

Amino-derivatives of Phenyldiphenylenemethane and the Corresponding Carbinol. ALFRED GUYOT and M. GRANDERYE (*Bull. Soc. chim.*, 1905, [iii], **33**, 198—205. Compare Abstr., 1901, i, 569; 1903, i, 748, and Ullmann and Wurstemberger, Abstr., 1904, i, 154).—*as*-Tetramethyldiaminophenyldiphenylenemethane, produced together with the *o*-hydroxy-leuco-base of malachite-green (Fischer, Abstr., 1881, 587) by diazotising the *o*-amino-leuco-base of malachite-green in sulphuric acid and then heating at 100°, melts at 158° (compare Abstr., 1903, i, 748).

Tetramethyldiaminophenyl-m-*methyldiphenylenemethane*,

$$NMe_2\cdot C_6H_4\cdot CH<\begin{matrix}C_6H_3\cdot NMe_2\\ |\\ C_6H_3Me\end{matrix},$$

similarly prepared from Noelting's base (Abstr., 1891, 727, and 1892, 187), having the constitution $CH(C_6H_4\cdot NMe_2)_2\cdot C_6H_3Me\cdot NH_2$ by diazotisation, forms small, white crystals. melts at 142°, and is slightly soluble in alcohol and ether, more so in benzene. On oxidation, it furnishes a dull violet dye. *Tetramethyldiaminophenyl*-m-*nitrodiphenylenemethane*, similarly prepared from a *nitro*-base which will be described in a future paper, crystallises in slender, brilliant, orange-yellow needles, melts at 170°, resembles the foregoing in solubility, and gives a blue dye on oxidation.

Tetramethyldiaminophenylphenylenenaphthylenemethane, similarly prepared from the *base* $NMe_2\cdot C_6H_4\cdot CH<\begin{matrix}C_6H_4\cdot NMe_2\\ |\\ C_{10}H_6\cdot NH_2\end{matrix}$, to be described in a future paper, forms slender, white needles, melts at 225—226°, and is soluble in benzene and scarcely so in alcohol and ether. T. A. H.

Desmotropic Compounds. HEINRICH GOLDSCHMIDT (*Zeit. Elektrochem.*, 1905, **11**, 5—7).—Dimroth (this vol., i, 98), from his experiments on the velocity of the conversion of methyl 5-hydroxy-1-phenyl-1 : 2 : 3-triazole-4-carboxylate into its ketonic form, has drawn the conclusion that the reaction only affects the non-dissociated molecules and does not take place between the ions. Owing to the fact that the non-dissociated molecules are in equilibrium with the ions, however, the product of the concentrations of the ions is proportional to the concentration of the non-dissociated molecules, and the velocity of reaction, which Dimroth has shown to be proportional to the latter, is therefore proportional to the former. Hence the experiments cannot decide whether the change is ionic or not. T. E.

[2 : 2′-Diamino-4 : 4′-oxalotoluidide.] FARBWERKE VORM. MEISTER LUCIUS, & BRÜNING (D.R.-P. 156177).—*m*-Tolylenediamine combines with oxalic acid at 100—225° to form 2 : 2′-*diamino*-4 : 4′-*oxalotoluidide*, $C_2O_2(NH{\cdot}C_6H_3Me{\cdot}NH_2)_2$, which separates as an amorphous, yellow powder melting at 180—220°, according to the mode of precipitation. It is insoluble in water and dissolves sparingly in hot alcohol to a yellow solution with slight green fluorescence. Azo-dyes may be prepared from the tetrazonium compound.

On fusing diamino-oxalotoluidide with sulphur at 80—140°, hydrogen sulphide is evolved and the reaction then ceases, but on heating further, condensation takes place at 170° and a new *compound* is obtained, which dyes a fast yellow shade in a sodium sulphide bath. C. H. D.

Formation of Heterocyclic Compounds from Hydrazine Derivatives. XVIII. Action of Ammonia on Tetrabromobenzylideneazine. ROBERT STOLLÉ (*J. pr. Chem.*, 1905, [ii], **71**, 30—33. Compare Abstr., 1903, i, 721; 1904, i, 102, 200, 453, 626, 627, 694—697; this vol., i, 94—97).—The action of ammonia on a cooled solution of tetrabromobenzylideneazine in carbon tetrachloride leads to the formation of a benzylidene derivative of 3 : 6-diphenyl-1 : 4-dihydrotetrazine and benzylideneazine.

The *benzylidene* derivative, $N\left\langle\begin{array}{c}CPh{:}N\\ -CHPh-\\ N{:}CPh\end{array}\right\rangle N$, is formed also when 3 : 6-diphenyl-1 : 4-dihydrotetrazine is shaken with benzaldehyde and dilute sulphuric acid. It crystallises in needles, melts at 207°, is soluble in alcohol or carbon tetrachloride, but not in water, and yields the dihydrotetrazine when a current of steam is passed through a suspension of it in dilute sulphuric acid. G. Y.

Action of Dicyanodiamide on the Primary Aromatic Amine Hydrochlorides. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and F. PERRIN (*Bull. Soc. chim.*, 1905, [iii], **33**, 205—207).—The authors find that in the preparation of phenyldiguanides by the action of dicyanodiamide (cyanoguanidine) on aniline hydrochloride, it is unnecessary to heat the reagents, dissolved in alcohol, in closed vessels, since

the reaction takes place when the two reagents are fused together over an oil-bath (compare Smolka and Friedrich, Abstr., 1888, 830).

p-*Hydroxyphenyldiguanide hydrochloride*,

$$NH_2\cdot C(NH)\cdot NH\cdot C(NH\cdot C_6H_4\cdot OH)\colon NH,HCl,$$

similarly prepared, melts at 203—204°; the *picrate* melts at 200—201°. p-*Anisyldiguanide hydrochloride* melts at 221—222° and the *picrate* at 193—195°.

The o- and p-*phenetyldiguanide hydrochlorides* melt respectively at 183—184° and 209—210°, and the corresponding *picrates* at 161—162° and 182—183° respectively. The *diguanide* derived from antipyrine yields a *picrate* melting and decomposing at 137—138°. These hydrochlorides, on treatment with silver oxide, furnish the *diguanides*, which are strongly alkaline substances, very soluble in water. T. A. H.

[o-Hydroxyazo-derivatives of α-Naphthylamine.] Badische Anilin & Soda-Fabrik (D.R.-P. 156440).—Whilst it is not possible to substitute hydroxyl for the sulpho-group in diazobenzene-o-sulphonic acid and its homologues by means of alkaline compounds, the reaction takes place readily in the case of the di- and poly-sulphonic acids of α-naphthylamine. The diazo-compounds of α-naphthylamine-2 : 4- and -2 : 5-disulphonic acids, or of α-naphthylamine-2 : 4 : 6- or -2 : 4 : 7-trisulphonic acids, react in the cold with alkali or alkaline earth acetates or carbonates, or with alkali nitrites, the sulpho-group being replaced by hydroxyl. The diazohydroxy-compounds thus obtained do not combine readily, but yield stable brown or violet dyes with β-naphthol. Subsequent treatment with chromium salts produces fast dark blue or black shades. C. H. D.

Limits of Coupling of Diazobenzene with Aniline. Léo Vignon (*Compt. rend.*, 1905, **140**, 91—93. Compare Abstr., 1904, i, 637, 1065).—Diazobenzene chloride does not condense with aminoazobenzene either in aqueous or alcoholic solution, but aniline condenses readily with diazoaminoazobenzene at 0° to form the *compound* $NPh\colon N\cdot C_6H_4\cdot N\colon N\cdot NHPh$, which crystallises from alcohol, melts at 112°, and on prolonged heating at 40° with aniline and aniline hydrochloride breaks down into aminoazobenzene (compare, however, Nietzki and Diesterweg, Abstr., 1888, 1080). Anilinebisdiazobenzene, $NH(N\colon NPh)_2$, prepared by the action of aniline on nitrosoacetanilide (Pechmann and Frobenius, Abstr., 1894, i, 283), when heated with aniline and aniline hydrochloride also yields aminoazobenzene, which appears to represent the limit of combination of diazobenzene with aniline (compare Abstr., 1904, i, 701). Attempts to prepare anilinebisdiazobenzene by the action of diazobenzene chloride on diazoaminobenzene or on aniline were unsuccessful. M. A. W.

[Azo-dyes from Alphylsulphonaminonaphthol Derivatives.] Badische Anilin- & Soda-Fabrik (D.R.-P. 156157).—Benzenesulphonic chloride reacts with 8-amino-α-naphthol-4-sulphonic acid in alkaline solution to form 8-*benzenesulphonamino-α-naphthol-4-sulphonic acid*, which is sparingly soluble. The quantity present may be determined by titration with a nitrophenyldiazonium salt in acetic acid

solution. The acid combines with diazotised picramic acid in slightly alkaline solution to form a crystalline *azo*-compound, which may be filtered, washed with sodium chloride solution, and dried. The dye dissolves in water to a violet solution, becoming red on the addition of alkalis. It yields fast bluish-black shades on subsequent treatment with chromium salts. Similar compounds are obtained from *o*- or *p*-toluenesulphonic chloride. C. H. D.

[Azo-dyes from Nitro-*m*-diamines.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 156352).—The diazosulphonic acids of the benzene and naphthalene series, such as the diazo-compounds of *p*-toluidine-*o*-sulphonic, *p*-chloroaniline-*m*-sulphonic, or *β*-naphthylamine-8-sulphonic acid, combine with nitrated *m*-diamines to form monoazo-dyes, which yield fast yellow or orange lakes with metallic salts. C. H. D.

Protective Action of Salt on Solutions of Proteids. WILHELM BILTZ (*Zeit. Elektrochem.*, 1904, **10**, 937—938).—Precipitated and well-washed hydrated ferric oxide or zirconium dioxide was shaken with solutions containing albumin and the quantity of albumin remaining in solution determined. A comparison of the results obtained with solutions containing salt and with dialysed solutions showed that the latter lost more albumin than the former. It is probable that a maximum protective action would be found at a certain concentration of salt, since a large excess of it precipitates albumin. The observations give an explanation of the fact that circulating blood does not coagulate. T. E.

Action of Pepsin on Albumin Precipitated by Heat in Presence of Acid. F. DISDIER (*J. Pharm. Chim.*, 1905, [vi], 21, 5—14).—The amount of acetic, tartaric, and oxalic acids in one per cent. solutions required for the precipitation of 100 grams of white of egg are 45, 57, and 48 c.c. respectively, numbers which are directly proportional to the equivalent weights of the acids. This rule also holds with nitric, butyric, and citric acids.

Using the most favourable proportions of hydrochloric acid for the digestion by pepsin of albumin precipitated by acid and for dissolved albumin, the author finds that, whilst the rates of digestion are equal with an acidity of 0·2 per cent., with an acidity of 0·1 per cent., 9 grams of precipitated albumin require 3 hours, the same weight of dissolved material requiring 12 hours for digestion. The difference in the acidity necessary for digestion is not due to acid combined with the precipitated albumin. G. D. L.

Oxidation of Proteids with Calcium Permanganate. II. Oxidation of Gelatin. FRIEDRICH KUTSCHER and MARTIN SCHENCK (*Ber.*, 1905, **38**, 455—459. Compare Abstr., 1904, i, 955).—The crystalline product obtained in the oxidation of gelatin with calcium permanganate, and formerly described as oxaluramide, proves to be oxamide. The filtrate contains guanidine in quantity corresponding with the arginine in the original material (compare also Loew, Abstr., 1885, 823). C. H. D.

Hydrolytic Cleavage of Proto-albumose. PHOEBUS A. LEVENE (*Proc. Amer. Physiol. Soc.*, 1904, xii—xiii; *Amer. J. Physiol.*, **13**).—Mixed with the hexone bases obtained from proto-albumose, a new material, $C_{12}H_{22}O_5N_4$, was obtained. The copper and silver salts were prepared and analysed; further investigation is in progress.

W. D. H.

Haloid Acid Salts of Peptones. KALLE & Co. (D.R.-P. 156399).—The irritant compounds produced in the action of haloid acids on peptones may be removed by washing the products with an alkali carbonate solution until neutral. The pure peptone salts yield non-irritant double salts with metallic haloids. C. H. D.

Protagon. E. R. POSNER and WILLIAM J. GIES (*Proc. Amer. Physiol. Soc.*, 1904, xxxv; *Amer. J. Physiol.*, **13**).—Further facts in favour of the view that protagon is not a chemical unit. W. D. H.

Absorptiometric Estimation of the Amount of Nitric Oxide combined by Unit Weight of Methæmoglobin. GUSTAV VON HÜFNER and B. REINBOLD (*Chem. Centr.*, 1905, i, 374; from *Arch. Anat. Physiol.*, *physiol. Abth.*, 1904, 391—395).—Methæmoglobin solutions take a purplish-red colour with nitric oxide (Hüfner and Otto); Hüfner and Külz state that the spectroscopic appearances of such a solution are the same as those of a solution obtained by passing a stream of nitric oxide through a solution of carboxyhæmoglobin. It is now shown that the volume of nitric oxide per gram of pigment is almost twice as great as that of carbon monoxide united to each gram of hæmoglobin.

W. D. H.

Hæmochromogen and Carbon Monoxide. GUSTAV VON HÜFNER and WILLIAM KÜSTER (*Chem. Centr.*, 1905, i, 373—374; from *Arch. Anat. Physiol.*, *physiol. Abth.*, 1904, 387—390).—Hæmochromogen was prepared from aceto-hæmin by reduction with potassium hydrosulphide; this combines with carbon monoxide, like hæmoglobin, in the proportion of 1 molecule of the gas per atom of iron.

W. D. H.

Spectroscopic Characters of Hæmatoporphyrin. ARTHUR SCHULZ (*Chem. Centr.*, 1905, i, 373; from *Arch. Anat. Physiol.*, *physiol. Abth.*, 1904, 271—286).—Hæmatoporphyrin, prepared by Nencki and Zaleski's methods, dissolved in alcohol shows five spectroscopic bands; the positions and relative intensities of these are described, as also are the changes which occur in them with different concentrations, or on the addition of such reagents as acids, alkalis, and zinc chloride.

W. D. H.

Organic Chemistry.

Some Constants of Pure Methane. The Action of Solid Methane on Liquid Fluorine. Henri Moissan and G. Chavanne (*Compt. rend.*, 1905, **140**, 407—410).—Pure methane, prepared by the action of water on aluminium carbide (compare Abstr., 1894, ii, 450) in a vessel from which all air had been removed, and purified by liquefying and then solidifying in a vacuum (compare Abstr., 1903, ii, 642), has a sweet and slightly alliaceous odour, a density 0·5540 to 0·5554 at 0° and under 760 mm. pressure; Thomson gives 0·558, and Schloesing 0·558 (compare Abstr., 1896, i, 401); it solidifies to a colourless, transparent, vitreous mass at the temperature of liquid air, and after a few moments crystallises in white needles, melting at −184° to a colourless liquid boiling at −164° under 760 mm. pressure; Olszewski gives −185·8° and −164° for the same constants (compare Abstr., 1885, 860).

When a closed tube containing solid methane is opened under liquid fluorine at −187°, there is a violent explosion accompanied by incandescence, the glass vessels being reduced to powder. The energy of the reaction is comparable with that which occurs between solid fluorine and liquid hydrogen (compare Abstr., 1903, ii, 360), and affords a further instance of the persistency of chemical affinity at very low temperatures. M. A. W.

Light Petroleum, Vaselin Oil, and Vaselin. Paul Adams (*Bull. Soc. chim.*, 1905, [iii], **33**, 274—283).—The author asserts that much of the light petroleum of commerce consists of the liquid hydrocarbons produced by "cracking" petroleum residues. A number of samples of light petroleum prepared about 1897 by the distillation of crude petroleum were examined. They absorbed quantities of bromine varying from 10 to 140 per cent. by weight, and lost this property after treatment with sulphuric acid. A crude light petroleum obtained by "cracking" petroleum residues, distilled between 60° and 135°, had a sp. gr. 0·712, absorbed 60 per cent. by weight of bromine, and when shaken with sulphuric acid, 21·15 per cent. was dissolved and the acid became black. A crude light petroleum obtained by fractional distillation of crude petroleum without "cracking" possessed a slight yellow colour, was dichroic, distilled between 40° and 130°, had a sp. gr. 0·675, absorbed 0·6 per cent. of its weight of bromine, forming a white precipitate and evolving hydrogen bromide. Sulphuric acid decolorised the material and itself became brown. A specimen of "gasolin," prepared from the foregoing by washing first with sulphuric acid and then with a solution of sodium hydroxide, distilled between 30° and 85°, had a sp. gr. 0·64, and did not react with mercury hydrogen sulphate or immediately with bromine in the cold.

A sample of vaselin oil, distilled unchanged between 335° and 440°, did not react with bromine in the cold and was not sensibly diminished in volume by agitation with sulphuric acid.

Vaselin should consist of the decolorised and deodorised residue of American petroleum after distilling off all products volatile below 360°, with the addition of from 2 to 5 per cent. of hard paraffin. On distillation, the constituents of vaselin undergo decomposition, and the products are crystalline paraffins, liquid hydrocarbons, and small quantities of gas, the two latter being partially ethylenic (compare Engler, Abstr., 1898, i, 165). The hard paraffin slowly separates when the distillate is kept. The author concludes that no hard paraffin exists already formed in vaselin. A list of the requirements to which vaselin should conform is given in the original. T. A. H.

Reaction distinguishing between Primary, Secondary, and Tertiary Alcohols. PAUL SABATIER and JEAN B. SENDERENS (*Bull. Soc. chim.*, 1905, [iii], **33**, 263—264. Compare Abstr., 1903, i, 393, 453, 454).—The authors utilise the characteristic products obtained from these different classes of alcohols as the result of their catalytic decomposition by metallic copper at 300° to distinguish between them, and an apparatus suitable for this purpose is described. The aldehydes produced under these conditions from primary alcohols are detected by means of magenta decolorised with sulphurous acid; the ketones obtained from secondary alcohols, by the formation of a precipitate with a solution of semicarbazide hydrochloride in presence of potassium acetate; and the liquid olefinic hydrocarbons furnished by tertiary alcohols (except trimethylcarbinol, which yields a gas), by their property of immediately decolorising bromine. T. A. H.

Fusibility in the Series of Normal Di-primary Glycols. LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1904, 1142—1149).—It is shown that so far as fusibility, as measured by melting point, is concerned this series consists of two partial series constituted by (*a*) those terms having an even number of carbon atoms, and (*b*) those having an odd number of carbon atoms. The data for the first of these partial series is fairly complete, and in this fusibility diminishes as the series is ascended. The differences between the melting points of consecutive pairs from C_2 to C_8 are 28°, 24°, and 23° respectively, and between C_8 and C_{10}, 8°. T. A. H.

Solubility of Metallic Hydroxides in Glycerol. ARTHUR MÜLLER (*Zeit. anorg. Chem.*, 1905, **43**, 320—325).—Definite weights of glucinum nitrate, aluminium nitrate, chrome alum, ferrous ammonium sulphate, ferric chloride, ceric ammonium nitrate, cerous ammonium nitrate, and neodymium magnesium nitrate respectively were dissolved in water, mixed with glycerol, and then agitated after the addition of ammonia. The behaviour of the resulting solutions on heating and on dilution with water is recorded. Glucinum and ceric hydroxides were insoluble, aluminium and chromium hydroxides sparingly soluble, and the other hydroxides easily soluble under the conditions used.

A. McK.

Basic Properties and the Quadrivalence of Oxygen. DOUGLAS McINTOSH (*J. Amer. Chem. Soc.*, 1905, **27**, 26—29).—Archibald and

McIntosh (Trans., 1904, **85**, 919) have shown that in certain compounds of the ethers and alcohols with hydrogen chloride the valency of the oxygen may be assumed to be as high as twelve. In view of this result, compounds of methyl ether and methyl alcohol with hydrogen bromide and hydrogen iodide have been prepared. These compounds are white, crystalline solids, almost insoluble in the ether or alcohol, but readily soluble in the liquefied acid used in their preparation; their formation is accompanied by the development of a large amount of heat. The *compound* $(CH_3)_2O,HI$ melts at $-15°$, the *compound* $CH_3{\cdot}OH,HI$ at $-48°$, the *compound* $(CH_3)_2O,HBr$ at $-22°$, and the *compound* $CH_3{\cdot}OH,HBr$ at $-14°$. In all these cases the oxygen is quadrivalent, and hence the experiments afford no further evidence as to the possibility of oxygen existing with a valency of eight or twelve. E. G.

Quadrivalent Oxygen. EDMOND E. BLAISE (*Compt. rend.*, 1905, **140**, 661—663. Compare this vol., ii, 111).—By the action of zinc on iodine in presence of ethyl ether, a crystalline compound of the formula $Zn(OEt_2I)_2$ is obtained. It is less stable than the corresponding magnesium compound (*loc. cit.*), but reacts with benzoyl chloride in a similar manner, giving rise to ethyl iodide, ethyl benzoate, and zinc chloride. When the diethyl ether groups in this compound are replaced by methyl amyl ether, the products of the reaction with benzoyl chloride are methyl iodide and amyl benzoate. The group with the smaller number of carbon atoms thus enters into combination with the iodine. If one of the ether groups is cyclic and has one of the carbon atoms attached directly to the oxygen atom, the reaction with benzoyl chloride is different. Hydrogen chloride is produced and the benzoyl group enters into combination with one of the carbon atoms of the nucleus.

Acetals give rise to analogous zinc iodine compounds and these react with benzoyl chloride in a similar manner. When ethyl orthoformate is added in small portions at a time to an ethereal solution of the compound $Hg(OEt_2I)_2$, a substance having the constitution

$$Mg[OEtI{\cdot}CH(OEt)_2]_2$$

separates in well-formed crystals. It reacts energetically with benzoyl chloride, the products being ethyl iodide, formate, and benzoate. The compounds which the ethers, acetals, and ortho-esters form with iodine and magnesium (or zinc) are thus all of the same type. Their properties and behaviour towards benzoyl chloride indicate the presence of quadrivalent oxygen atoms. The compounds which the esters form with iodine and magnesium are of a different type, $(RCO_2R')_6MgI_2$, and behave differently towards benzoyl chloride. H. M. D.

Action of Hydrogen Cyanide on Epiethylin (Ethyl Glycide Ether). ROBERT LESPIEAU (*Compt. rend.*, 1905, **140**, 436—437).—Bromoethylin ($\alpha\alpha$-bromoethoxyhydrin), obtained by the action of phosphorous bromide on glycerol α-monoethyl ether, boils at 197° under 760 mm. pressure and reacts with potassium hydroxide to form epiethylin (ethyl

glycide ether), $O\textless\begin{matrix}CH\cdot CH_2\cdot OEt \\ | \\ CH_2\end{matrix}$, which combines with hydrogen cyanide, slowly at the ordinary temperature, or more rapidly at 70°, to form *a-cyano-β-hydroxy-γ-ethoxypropane*, $OEt\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot CN$, a colourless liquid, soluble in water, boiling at 243—245° under 760° mm. pressure, and yielding, on saponification with hydrochloric acid in the presence of alcohol, *ethyl β-hydroxy-γ-ethoxybutyric acid*,

$$OEt\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot CO_2Et,$$

boiling at 120—121° under 13 mm. pressure, and converted by the action of potassium hydroxide into the potassium salt of the corresponding acid, *β-hydroxy-γ-ethoxybutyric acid*,

$$OEt\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot CO_2H,$$

which is a syrup and loses 1 mol. H_2O on distillation, forming an unsaturated acid. *β-Chloro-a-cyano-γ-ethoxypropane*,

$$OEt\cdot CH_2\cdot CHCl\cdot CH_2\cdot CN,$$

obtained by the action of phosphorus pentachloride on the corresponding hydroxy-compound, boils at 105° under 19 mm. pressure, from which *β-chloro-γ-ethoxybutyric acid*, $OEt\cdot CH_2\cdot CHCl\cdot CH_2\cdot CO_2H$, boiling at 144—145° under 14 mm. pressure and melting at 2°, and its *amide*, melting at 64°, are readily obtained by the ordinary methods.

M. A. W.

Preparation of Nitro-products of Organic Compounds. J. Matuschek (*Chem. Zeit.*, 1905, **29**, 115).—Ethyl nitrite is formed by the action of sodium nitrite on magnesium sulphate in presence of ethyl alcohol, since magnesium nitrite is unstable, especially when its solution is heated. The change $Mg(NO_2)_2 + H_2O = Mg(OH)_2 + NO_2 + NO$ is undergone, whilst the nitrogen peroxide thus formed acts on the ethyl alcohol present. A similar result was obtained with iron salts.

Phenols, amines, and aldehydes may be nitrated in a similar manner, the solvent used in these cases being ether.

Nitrobenzene is formed when a little ferric chloride is added to a mixture of powdered sodium nitrite and benzene. A. McK.

Ethylene Xanthate and Ethylene Thiocarbonate. P. Frassetti (*Ber.*, 1905, **38**, 488—492. Compare Welde, *J. pr. Chem.*, 1877, [ii], **15**, 55).—Alcoholic potash converts ethylene xanthate into Bender's salt, ethylene thiocarbonate, and ethyl alcohol,

$$C_2H_4(S\cdot CS\cdot OEt)_2 + KOH = KS\cdot CO\cdot OEt + C_2H_4CS_3 + EtOH.$$

The yield of ethylene thiocarbonate is theoretical when only one equivalent of alkali is employed. It crystallises from a mixture of alcohol and ether in pale yellow, rhombic needles melting at 39°. Ethylene disulphide is obtained when the alcoholic filtrate from Bender's salt is exposed to the air, and on reduction with sodium amalgam it is converted into the sodium salt of ethylene hydrosulphide, $C_2H_4(SNa)_2$. An ethereal solution of ethyl xanthate reacts with alcoholic ammonia, yielding xanthamide and ethylene thiocarbonate.

Ethylene thiocarbonate and alcoholic potash yield Bender's salt and the potassium salt of ethylene hydrosulphide,

$$C_2H_4CS_3 + EtOH + 3KOH = KS\cdot CO\cdot OEt + C_2H_4S_2K_2 + 2H_2O.$$

J. J. S.

The Non-existence of Two Stereoisomerides of Ethyl $\alpha\beta$-Dioximidobutyrate. Louis Bouveault and André Wahl (*Compt. rend.*, 1905, **140**, 438—440; *Ber.*, 1904, **38**, 926—931).—Ethyl $\alpha\beta$-dioximidobutyrate, obtained by the action of hydroxylamine hydrochloride on ethyl diketobutyrate (compare Abstr., 1904, i, 556), crystallises from ether and light petroleum in large, transparent crystals melting at 160—162°, and the same compound is obtained, together with *iso*nitrosomethyl*iso*oxazolone, melting at 159°, when pure ethyl *iso*nitrosoacetoacetate reacts with hydroxylamine in acid or alkaline solution. Ethyl $\alpha\beta$-dioximidobutyrate is partially converted to *iso*nitrosomethyl*iso*oxazolone by the action of hydrogen chloride in ethereal solution, but the two constituents of the solid mixture are readily separated by the action of water, which dissolves the *iso*oxazolone, but not the dioxime.

The *mono-acetyl* derivative of ethyl $\alpha\beta$-dioximidobutyrate, prepared by the action of acetyl chloride on the dioxime, melts at 149°, and the *diacetyl* derivative prepared by the action of acetic anhydride on the dioxime or the mono-acetyl derivative melts at 53—54°.

From these results, the author concludes that there is only one ethyl $\alpha\beta$-dioximidobutyrate, the *syn-* and *amphi*-stereoisomerides melting at 142° and 132° respectively, described by Nussberger (Abstr., 1892, 1175), and the compound melting at 140°, described by Cerésole and Köckert (Abstr., 1884, 1120), being mixtures of the dioxime and the *iso*oxazolone, whilst the *amphi*-diacetyl derivative melting at 119—120°, described by Nussberger, was probably an impure mono-acetyl derivative. M. A. W.

Marckwald's Asymmetric Synthesis of Optically Active Valeric Acid. S. Tijmstra (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, **7**, 465—468).—Methylethylmalonic acid may be converted into valeric acid [α-methylbutyric acid] at 100° at the ordinary pressure if the carbon dioxide eliminated is removed from the sphere of action.

The author modifies Marckwald's asymmetric synthesis (Abstr., 1904, i, 221) by heating the hydrogen brucine salt of methylethylmalonic acid with continual evacuation at 120° instead of heating at the melting point, 155°, as Marckwald did. In this way, the racemisation phenomena, supposed by Marckwald to occur under the conditions employed by him, are less marked. The valeric [α-methylbutyric] acid obtained had $[\alpha]_D - 4{\cdot}3°$, which corresponds with 25·8 per cent. of *l*-valeric acid, whereas Marckwald's product had $\alpha_D - 1{\cdot}7°$ ($l = 1$), which corresponds with about 10 per cent. of *l*-acid. A. McK.

Direct Fixation of Organo-magnesium Derivatives on the Ethylenic Linking of Unsaturated Esters. Edmond E. Blaise and A. Courtot (*Compt. rend.*, 1905, **140**, 370—372).—Ethyl methylacrylate, readily prepared by the action of diethylaniline on ethyl α-bromo*iso*butyrate, reacts with magnesium methyl iodide at 0° to form a condensation product, which, on decomposition with water, yields a mixture of dimethylpropenylcarbinol (compare Chupotsky and Mariutza, Abstr., 1890, 727) boiling at 119° and γ-methylpentane-β-one

boiling at 116°, having an agreeable odour similar to that of camphor, and forming an oxime boiling at 89° under 20 mm. pressure, a phenyl hydrazone boiling at 153° under 10 mm. pressure, and a crystalline semicarbazone melting at 96° and identical with the ketone obtained synthetically by the hydrolysis of ethyl methylethylacetoacetate. Magnesium ethyl iodide reacts with ethyl methylacrylate, but the sole product of the reaction is diethylpropenylcarbinol, boiling at 162°, whilst magnesium methyl iodide and ethyl $\alpha\alpha$-dimethylacrylate yield dimethyl*iso*butenylcarbinol boiling at 138°, $\beta\delta$-dimethyl-$\Delta^{\alpha\gamma}$-pentadiene boiling at 90°, and a small quantity of a ketone, probably $\beta\beta$-dimethylpentane-δ-one, yielding a semicarbazone melting at 124°. M. A. W.

Influence of Atmospheric Moisture on the Oxygen Absorption of Oils. III. WALTER LIPPERT (*Zeit. angew. Chem.*, 1905, **18**, 94—95).—Various oils examined dried more quickly in a dry atmosphere than in a moist one. When traces of manganese are present, the oil dries better in a moist atmosphere than in a dry one.

A. McK.

Mechanism of the Ethyl Acetoacetate Syntheses. LUDWIG CLAISEN (*Ber.*, 1905, **38**, 709—719).—A theoretical paper, discussing the fact that in preparing ethyl acetoacetate a better yield is obtained by using metallic sodium than by means of sodium ethoxide (compare Michael, Abstr., 1901, i, 123). W. A. D.

Lactone of Triacetic Acid. ANTONIO TAMBURELLO (*Chem. Centr.*, 1905, i, 348; privately printed, Palermo, July 1904).—The results recorded agree with the observations of Dieckmann and Breest (Abstr., 1904, i, 846).

The formation of mono- and tri-phenylhydrazones agrees with a ketonic structure for the lactone, $O<\begin{matrix}CO-CH_2\\CMe:CH\end{matrix}>CO$, the inactivity of the phenylhydrazone towards *o*-phenylenediamine showing that the two carbonyl groups are not in the ortho-position. The acidity, formation of salts, red colour reaction with ferric chloride, and formation of *O*-ethers by means of diazo-methane or -ethane, or from ethyl iodide and the silver salt, agree with the desmotropic structure, $O<\begin{matrix}C(OH):CH\\CMe{=}CH\end{matrix}>CO$. The monobromo-derivative resembles the lactone, and like it must contain an unaltered methylene group and be either $O<\begin{matrix}CO-CH_2\\CMe:CBr\end{matrix}>CO$ or $O<\begin{matrix}CO-\!\!-\!\!-CH_2\\C(CH_2Br):CH\end{matrix}>CO$.

The *phenylhydrazone*, $C_{12}H_{10}O_3N_2$, prepared by means of diazobenzene acetate, forms red needles from alcohol or benzene, melts at 185—186°, and with phenylhydrazone (2 mols.) yields the *triphenylhydrazone*, $C_6H_4O(N_2HPh)_3$, which forms yellow leaflets from alcohol or benzene, melts at 174—175°, and gives the osotetrazone reaction with ferric chloride. Nitrous vapours form, with a cold ethereal suspension of the lactone, a *nitro*-compound, $C_6H_5O_3{\cdot}ON{\cdot}C_6H_5O_3NO_2$, which forms needles decomposing explosively at 165—166°.

Diazomethane produces the *O-methyl ether*, which forms needles soluble in cold alcohol or ether and melts at 81—82°; the *ethyl ether*, prepared in similar manner or from the silver salt and ethyl iodide, melts at 59—60°. With diazomethane, the monobromolactone gives the *O-methyl ether*, which crystallises from benzene in plates, melts at 153—154°, and gives no coloration with ferric chloride. G. D. L.

Variations in the Crystallisation of Potassium Hydrogen Succinate due to the Presence of Other Metallic Compounds in the Solution. ALEXANDER T. CAMERON (*Proc. Roy. Soc. Edin.*, 1905, **25**, 449—451).—From a solution obtained by boiling potassium hydrogen succinate with freshly precipitated chromic hydroxide, crystals of potassium hydrogen succinate and, later, a green, crystalline powder are deposited. On concentrating to about half the volume and keeping, dark green crystals having the form of oblique elliptical double cones possessing monoclinic symmetry are obtained. The percentage of chromium in different preparations varies considerably, but is always less than 1 per cent. Since potassium hydrogen succinate crystallises in monoclinic crystals, the author suspects that the green crystals represent potassium hydrogen succinate containing some chromium compound, possibly in solid solution, this bringing about a modification in the external surfaces of the crystals. Similar crystals with curved faces have been obtained from solutions of the succinate after treatment with aluminium hydroxide, ferric chloride, or copper carbonate.

Chromic hydroxide dissolves readily in potassium hydrogen malate, and the solution deposits crystals similar to the above. H. M. D.

Methyl Itaconate. RICHARD ANSCHÜTZ [and FERDINAND HAAS] (*Ber.*, 1905, **38**, 690—693).—Methyl itaconate has hitherto only been obtained as a liquid which slowly undergoes polymerisation; when prepared from pure silver itaconate and methyl iodide, it readily solidifies, and, after recrystallisation from methyl alcohol, melts at 38° and boils at 108° under 11 mm. or at 208° under 760 mm. pressure. It forms monoclinic crystals [$a:b:c = 1.7372:1:1.0094$; $\beta = 100°24'$], has a normal molecular weight in ethereal solution and in the state of vapour, and does not polymerise after several months.

W. A. D.

Lactyl-lactyl-lactic Acid and the Dilactide of Inactive Lactic Acid. EMIL JUNGFLEISCH and MARCEL GODCHOT (*Compt. rend.*, 1905, **140**, 502—505).—*Lactyl-lactyl-lactic acid*,

$$OH\cdot CHMe\cdot CO\cdot O\cdot CHMe\cdot CO\cdot O\cdot CHMe\cdot CO_2H,$$

obtained together with dilactide when lactic acid is distilled at 230—250° under 25 mm. pressure, is much more readily soluble in ether than the dilactide, crystallising in tufts of small, colourless needles melting at 39° and boiling at 235—240° under 20 mm. pressure, and readily soluble in chloroform, benzene, or acetic acid. It dissolves readily in water, and the aqueous solution is hydrolysed slowly at the ordinary temperature or rapidly at 100°, forming 3 mols.

of lactic acid; by the action of gaseous ammonia, it is decomposed into lactamide and ammonium lactate according to the equation:

$$OH\cdot CHMe\cdot CO\cdot O\cdot CHMe\cdot CO\cdot O\cdot CHMe\cdot CO_2H + 3NH_3 = 2OH\cdot CHMe\cdot CO\cdot NH_2 + OH\cdot CHMe\cdot CO_2\cdot NH_4.$$

The hydrolysis of racemic dilactide to lactic acid occurs through the intermediate formation of lactyl-lactic acid, and this explains the slow deposition of zinc lactate from a solution of dilactide neutralised by zinc oxide observed by Wislicenus; the solution contained zinc lactyl-lactate, which was slowly hydrolysed into lactic acid and zinc lactate.

M. A. W.

Electro-synthesis among the Cyano-derivatives. Celso Ulpiani and G. A. Rodano (*Atti R. Accad. Lincei*, 1905, [v], **14**, i, 110—114).—Electrolysis of an aqueous solution of ethyl sodiocyanomalonate yields a *compound* of the constitution

$$CN\cdot C(CO_2Et)_2\cdot C(CO_2Et)_2\cdot CN,$$

which separates from aqueous alcohol in white crystals ($+1\frac{1}{2}H_2O$) melting at 56—57° and is readily soluble in alcohol, ether, chloroform, or benzene. It has the normal molecular weight in freezing benzene. The best yield is obtained with a 1 per cent. solution of the sodium salt of ethyl cyanomalonate and a current intensity of 0·2—0·25 amperes.

T. H. P.

Formaldehyde Sodium Hydrogen Hyposulphite. Luc. Baumann, Georges Thesmar, and Jos. Frossard (*Bull. Soc. Ind. Mulhouse*, 1904, **74**, 348—360. Compare Prud'homme, this vol., ii, 157).—Zinc dust and sulphuric acid are added to a mixture of sodium hydrogen sulphite and ice. The zinc is then removed by the addition of sodium hydrogen carbonate, and from the filtrate so-called "sodium hyposulphite" is precipitated by the addition of brine (compare Bernthsen and Bazlen Abstr., 1900, ii, 203). A solution of this in 40 per cent. formaldehyde, when cooled, deposits a crystalline product having a composition approximately represented by the formula $Na_2S_2O_4,2CH_2O,4H_2O$ (compare H. Schmid, *Bull. Soc. Ind. Mulhouse*, 1904, **74**, 63), which can be separated by fractional crystallisation from dilute alcohol into equal parts of formaldehyde sodium hydrogen sulphite and formaldehyde sodium hydrogen hyposulphite, $NaHSO_2,CH_2O,2H_2O$ (Zundel, *ibid.*, 49). The latter crystallises from water in large, transparent, monoclinic (?) prisms, melts at 63—64°, begins to lose water of crystallisation at 120°, at 125° evolves formaldehyde and hydrogen sulphide, and finally leaves a residue of sodium sulphide. Mineral acids decompose it with the formation of sulphur and hydrogen sulphide; alkalis regenerate sodium hyposulphite and formaldehyde, and sodium hydroxide followed by ammonia solution furnishes disodium hyposulphite and hexamethylenetetra-amine. The *lead* derivative is insoluble in water, but dissolves in dilute nitric or in acetic acid to form a strongly reducing solution. The compound can be applied as a reducing agent when warmed in presence of alkalis or sodium hydrogen sulphite and, in these circumstances, gives good results in the conversion of nitro-derivatives into the corresponding amines.

The authors consider that these observations confirm the validity of

the formula H_2SO_2 assigned by Schutzenberger to hyposulphurous acid (*Compt. rend.*, 1869, **69**, 196). T. A. H.

Constitution of Aldehydesulphurous Acid and Hyposulphurous Acid. KARL REINKING, ERICH DEHNEL, and HANS LABHARDT (*Ber.*, 1905, **38**, 1069—1080. Compare preceding abstract and this vol., ii, 240).—Hydroxymethanesulphonic acid, $OH \cdot CH_2 \cdot SO_3H$ (compare Müller, this Journal, 1874, 45), is best prepared by cautiously adding 50 per cent. sulphur trioxide to a cooled mixture of methyl alcohol and sulphuric acid monohydrate. The *sodium* salt crystallises in needles grouped in stellar aggregates and can be heated with acids and alkalis without change.

Aminomethyl hydrogen sulphite, $NH_2 \cdot CH_2 \cdot O \cdot SO_2H$, prepared by the interaction of formaldehyde, sodium hydrogen sulphite, and ammonia, forms colourless crystals decomposing at 193°; on reduction with zinc dust and acetic acid, *zinc aminomethylsulphoxylate* is formed. Both sodium hyposulphiteformaldehyde and formaldehydesulphoxylate form compounds with amines; *sodium* o-*toluidinoformaldehydesulphoxylate*, $C_7H_7 \cdot NH \cdot CH_2 \cdot O \cdot SONa,3H_2O$, has been analysed. It is clearly proved that hydroxymethanesulphonic acid and formaldehyde sulphurous acid are not identical. E. F. A.

Chloro-derivatives of Propyl and *iso*Propyl Formals. LÉON STAPPERS (*Bull. Acad. roy. Belg.*, 1904, 1161—1170. Compare Henry, Abstr., 1904, i, 364).—*Chloromethyl* iso*propyl ether*,

$$CH_2Cl \cdot OPr^{\beta},$$

obtained by the action of hydrogen chloride on formaldehyde in presence of *iso*propyl alcohol, is a colourless, mobile liquid with a pungent odour; it boils at 101—102° under 760 mm. pressure, has a sp. gr. 0·972 at 20° and n_D 1·41136 at 18°. It evolves hydrogen chloride on exposure to moist air.

*Chloromethyl α-chloro*iso*propyl ether*, $CH_2Cl \cdot O \cdot CHMe \cdot CH_2Cl$, similarly prepared, is a colourless liquid which boils at 162—164° under 763 mm. pressure and has a sp. gr. 1·197 at 20°.

The *iso*propyl formals and their derivatives may be obtained by the action of hydrogen chloride on formaldehyde in presence of 2 mols. of the appropriate *iso*propyl compound, or by the interaction of the latter with trioxymethylene in presence of ferric chloride (compare Arnhold, Abstr., 1887, 912).

s-*αα-Dichloro*iso*propyl formal*, $CH_2[O \cdot CHMe \cdot CH_2Cl]_2$, is a colourless, mobile liquid with a sharp, bitter taste; it boils at 227—228° under 758 mm. pressure, has a sp. gr. 1·150 at 20° and n_D 1·45607 at 20°. The isomeric s-*ββ dichloropropylformal*, $CH_2[O \cdot CH_2 \cdot CHCl \cdot CH_3]_2$, prepared from propylene β-chlorohydrin (Henry, Abstr., 1903, i, 725), boils at 228°, has a sp. gr. 1·145 at 20° and n_D 1·45307.

s-*Tetrachloro*iso*propyl formal*, $CH_2[O \cdot CH(CH_2Cl)_2]_2$, obtained by the action of trioxymethylene on *s*-glyceryl dichlorohydrin in presence of ferric chloride, melts at 51°, boils at 220° under 107 mm. pressure, is soluble in benzene or chloroform, and slightly so in light petroleum. It forms crystals belonging to the monoclinic system [$a : b : c =$

$2 \cdot 787 : 1 : 1 \cdot 384$; $\alpha = 82°50'$]. The *isomeric* compound,

$$CH_2[O \cdot CH_2 \cdot CHCl \cdot CH_2Cl]_2,$$

similarly obtained from *as*-glyceryl dichlorohydrin, is a colourless, viscid liquid having sp. gr. 1·370 and n_D 1·49399 at 20°. T. A. H.

Condensation of Methylethylacraldehyde with *iso*Butaldehyde. WILHELM MORAWETZ (*Monatsh.*, 1905, **26**, 127—132).—The *aldol*, $CHEt\colon CMe \cdot CH(OH) \cdot CMe_2 \cdot COH$, formed by the condensation of methylethylacraldehyde with *iso*butaldehyde in alcoholic potassium hydroxide solution, is a viscid, yellow oil, which boils at 130—140° under 11 mm. pressure, reduces ammoniacal silver solutions, and forms an *additive* compound with 1 mol. of bromine in chloroform solution. The *oxime*, $C_{10}H_{19}O_2N$, is a viscid, yellow oil, which boils at 160—170° under 18 mm. pressure; the *acetyl* derivative, $C_{12}H_{20}O_3$, is an oil which decomposes on distillation. When boiled with silver oxide and water, the aldol yields the *silver* salt of the corresponding hydroxy-acid, $C_{10}H_{17}O_3Ag$, which crystallises in glistening leaflets on concentration of the aqueous solution over sulphuric acid in a vacuum.

G. Y.

The Diphenylhydrazones of *l*-Arabinose and of Xylose. BERNHARD TOLLENS and A. D. MAURENBRECHER (*Ber.*, 1905, **38**, 500—501. Compare Neuberg, *Ber.*, 1904, **37**, 4618).—Müther and Tollens' statement (Abstr., 1904, i, 224) that *l*-arabinosediphenylhydrazone melts at 204—205° is confirmed. This hydrazone has also been obtained by the action of diphenylhydrazine on the products formed during the hydrolysis of cocoa beans. J. J. S.

***iso*Maltose.** EDUARD JALOWETZ (*Zeit. angew. Chem.*, 1905, **18**, 171).—The crystalline form and the appearance of maltosazone vary according to the mode of preparation (compare Ost, this vol., i, 22).

A. McK.

Reversion of Amylocellulose into Starch. EUGÈNE ROUX (*Compt. rend.*, 1905, **140**, 440—442).—Maquenne has shown that starch paste slowly reverts into amylocellulose (compare Abstr., 1903, i, 679; 1904, i, 17, 227, 228, 294, 800). In the present paper, the reaction is shown to be a reversible one between the temperatures of 0° and 150°; at the higher temperature, and in the presence of excess of water, the amylocellulose liquefies after 10 minutes, and on cooling forms a starch paste or jelly which is coloured blue by iodine; if, however, the heating is prolonged to about 3 hours, the solution on cooling deposits spherical granules of artificial starch, closely resembling the natural grains in their appearance under the microscope, and like them being coloured blue by iodine; they do not, however, form a jelly with boiling water. If the amylocellulose is heated with water at 150° for a longer period than 3 hours, amylodextrin is formed, which gives a yellow colour with iodine and breaks down on continued heating into dextrins and dextrose. Amylocellulose, natural and artificial starch are to be regarded as different condensa-

tion forms of the same fundamental chemical nucleus (compare Maquenne, Abstr., 1904, i, 294). M. A. W.

Optically Active Nitrogen Compounds. Miss M. B. Thomas and Humphrey O. Jones (*Proc. Camb. Phil. Soc.*, 1905, **13**, 33—34. Compare Trans., 1904, **85**, 223; 1905, **87**, 135).—*Phenylbenzylmethyl*iso*propylammonium iodide*, prepared by mixing methyl*iso*propylaniline with benzyl iodide in molecular proportions, melts at 133°. When this is treated with the calculated quantity of silver *d*-bromocamphorsulphonate in ethyl acetate solution and the product crystallised three times from ethyl acetate or water, l-*phenylbenzylmethyl*iso*propylammonium* d-*bromocamphorsulphonate* is obtained. In dilute aqueous solution, $[M]_D - 123°$. Subtracting the rotation due to the acid ion, the value of $[M]_D$ for the basic ion is obtained, $-393°$.

l-Phenylbenzylmethyl*iso*propylammonium iodide is obtained by precipitating the aqueous solution of the bromocamphorsulphonate by a solution of potassium iodide. It melts at 132° and crystallises in the tetragonal system, whereas the crystals of the inactive iodide belong to the oblique system, from which it is concluded that the latter must be a racemic compound. The active iodide is stable in alcoholic solution; it racemises quickly in chloroform solution. In absolute alcohol, $[M]_D - 428°$.

i-*Phenylbenzylmethyl*iso*amylammonium iodide* forms small prisms melting at 156°. On preparing the *d*-camphorsulphonate and crystallising from acetone, the salt of the lævo-base was obtained after twenty crystallisations, although not perfectly pure. It melts at 178—178·5°; in dilute aqueous solution, $[M]_D - 317°$, from which, for the basic ion, $[M]_D - 370°$ is calculated. The corresponding active iodide melts at 156°; in ethyl alcohol, $[M]_D - 478°$. It racemises in chloroform solution.

Substitution of *iso*propyl or *iso*amyl for the ethyl group in the phenylbenzylmethylethylammonium ion thus causes a change in the molecular rotation of more than 350° and 370° respectively. Substitution of these for the allyl group also increases the molecular rotation to a great extent, since for the phenylbenzylmethylallylammonium ion $[M]_D = 166°$. H. M. D.

Copper and Nickel Salts of some Amino-acids. Giuseppe Bruni (*Zeit. Elektrochem.*, 1905, 11, 93—94).—A claim for priority (see Bruni and Fornara, Abstr., 1904, i, 855, and H. Ley, this vol., i, 175). T. E.

Synthesis of Polypeptides. IX. Chlorides of the Aminc-acids and their Acyl Derivatives. Emil Fischer [with F. Reuter] (*Ber.*, 1905, **38**, 605—619. Compare Abstr., 1903, i, 465, 607, 799; 1904, i, 652, 771, 867, 890; this vol., i, 30, 31).—Two new reactions are described, namely, the preparation of amino-acid chlorides by the interaction of the acids with phosphorus pentachloride and acetyl chloride, and the splitting of the ring in diketopiperazine derivatives by means of dilute alkalis, which very much facilitate the synthesis of derivatives of polypeptides.

Thus, on shaking glycine anhydride with the equivalent quantity of normal sodium hydroxide, it is converted into the alkali salt of glycylglycine, and this, on further treatment with acid chlorides, such as benzoyl chloride, yields benzoylglycylglycine. Alanine anhydride acts in a similar manner, but leucinimide is only hydrolysed with great difficulty.

*Ethyl α-bromo*iso*hexoyldiglycylglycine*,

$$C_4H_9\cdot CHBr\cdot[CO\cdot NH\cdot CH_2]_3\cdot CO_2Et,$$

can be prepared either by the action of acetyl chloride and phosphorus pentachloride on α-bromo*iso*hexoylglycylglycine and subsequent combination of the chloride formed with ethyl glycine, or, still better, by the interaction of ethyl glycylglycine with the chloride of α-bromo*iso*hexoylglycine. It melts at 184·5° (corr.) and crystallises in stellar aggregates or clusters of colourless needles. The corresponding *α-bromo*iso*hexoyldiglycylglycine* melts at 168° (corr.), crystallises from alcohol in minute needles, and is converted by dilute ammonia into *leucyldiglycylglycine*,

$$C_4H_9\cdot CH(NH_2)\cdot CO[NH\cdot CH_2\cdot CO]_2\cdot NH\cdot CH_2\cdot CO_2H\ ;$$

this darkens at 215°, melts to a dark liquid at 233° (corr.), and gives the biuret reaction.

Hippuryl chloride, $COPh\cdot NH\cdot CH_2\cdot COCl$, is easily prepared by the action of acetyl chloride and phosphorus pentachloride on hippuric acid; it crystallises from acetyl chloride in colourless needles, becomes yellow at 125° and then dark red, and melts at a higher temperature. Alcohol or water converts the chloride into hippuric acid; with ethereal ammonia, hippuramide, melting at 183°, is formed. Hippuryl chloride reacts readily with ethyl glycine, either in ethereal or alkaline solution, forming the benzoylglycylglycine melting at 206°, described by Curtius and Wüstenfeld (Abstr., 1904, i, 833).

Leucyl chloride hydrochloride, $C_4H_9\cdot CH(NH_3Cl)\cdot COCl$, is prepared by the combined action of acetyl chloride and phosphorus pentachloride on leucine, special precautions being taken to exclude all traces of moisture, while the product is filtered and washed. The salt is relatively stable towards heat, but is decomposed at once by water into leucine and hydrogen chloride; it reacts with ethyl glycine in ethereal solution, forming *ethyl leucylglycine*, which was isolated as *leucylglycine anhydride*, $C_4H_9\cdot CH<{CO\cdot NH \atop NH\cdot CO}>CH_2$, crystallising in colourless needles and melting at 244°.

Alanyl chloride hydrochloride, $NH_3Cl\cdot CHMe\cdot COCl$, prepared as above, forms a colourless, crystalline mass which sinters about 110°. *α-Aminobutyryl chloride hydrochloride*, $CH_2Me\cdot CH(NH_3Cl)\cdot COCl$, forms well-defined crystals. E. F. A.

The Carbimide of Natural (*l*) Leucine. LOUIS HUGOUNENQ and ALBERT MOREL (*Compt. rend.*, 1905, **140**, 505—506. Compare this vol., wateī^S\.—Natural (*l*) leucine reacts with carbonyl chloride in toluene formed, wat 130° to form leucinecarbimide (compare Vittenet, Abstr., continued'56; 1900, i, 153), which, however, could not be isolated in a natural and: the *ethyl ester*, $CO{:}N\cdot CH(CO_2Et)\cdot CH_2\cdot CHMe_2$, obtained

together with *diethyl leucinecarbamide*,

$$CO[NH\cdot CH(CO_2Et)CH_2\cdot CHMe_2]_2,$$

boiling at 180—190° under 18 mm. pressure, by the action of carbonyl chloride in toluene solution at 130° on the ethyl ester of leucine (compare Fischer, Abstr., 1901, i, 192), is a colourless liquid boiling at 120—130° under 18 mm. pressure, having a disagreeable odour, and emitting irritating vapours; it reacts with alcohols to form urethanes, is insoluble in water, and soluble in benzene, ether, or chloroform. M. A. W.

Mercury Thiocyanate Complexes. MILES S. SHERRILL and S. SKOWRONSKI (*J. Amer. Chem. Soc.*, 1905, **27**, 30—47).—Sherrill (Abstr., 1903, ii, 534) has investigated the mutual relations of mercuric chloride, bromide, iodide, and cyanide to the corresponding potassium salts with special reference to the formation of complexes. This work has now been extended to mercuric thiocyanate.

The results of solubility, freezing point, and *E.M.F.* determinations have shown that in aqueous solution a complex salt, $K_2Hg(SCN)_4$, is formed. The same salt is produced when mercurous thiocyanate is treated with potassium thiocyanate, mercury being liberated.

A comparison of the stability constants of the mercuric complexes shows that the relative tendency of the halogens and of cyanogen and thiocyanogen groups to form complexes increases in the order Cl, Br, SCN, I, CN, a result which agrees with the observations of Grossmann (Abstr., 1904, i, 147) and Bodländer and Eberlein (Abstr., 1904, ii, 401).

The solubility product of mercurous thiocyanate, $[Hg^{++}][SCN^-]^2$, has been deduced from the results of experiments described in this paper and found to be $1\cdot8 \times 10^{-20}$. E. G.

Aminoacetone. SIEGMUND GABRIEL (*Ber.*, 1905, **38**, 752—753. Compare Abstr., 1893, i, 734; 1903, i, 13; Alexander, this vol., i, 92).—The action of hydrogen cyanide on aminoacetone hydrochloride at the ordinary temperature leads to the formation of a *substance*, $(C_4H_6N_2)_n$, which is obtained in crystalline nodules or thin rhomboids, sinters at 180°, melts and decomposes at 190—192°, volatilises without melting when slowly heated, and when boiled with water undergoes decomposition into its generators. G. Y.

***iso*Cysteine and *iso*Cystine.** SIEGMUND GABRIEL (*Ber.*, 1905, **38**, 630—646).—γ-Hydroxypropylphthalimide, melting at 75° (compare Abstr., 1890, 472), is converted, on oxidation with potassium dichromate, into *phthalyl-β-alanine*, $C_8H_4O_2\colon N\cdot CH_2\cdot CH_2\cdot CO_2H$, melting at 150—151°; the *ethyl* ester separates in flat needles melting at 73·5°. The corresponding *phthalyl-α-alanine*, $C_8H_4O_2\colon N\cdot CHMe\cdot CO_2H$, forms colourless needles melting at 160—162° and an *ethyl* ester melting at 61—63° (compare Andreasch, Abstr., 1904, i, 895). It was found impossible to brominate either of the phthalylalanines.

Dihydrouracil, $CH_2<\begin{matrix}CH_2\cdot NH\\CO-NH\end{matrix}>CO$, may be prepared either by the

interaction of β-alanine hydrochloride, obtained from the phthalyl derivative, dissolved in normal potassium hydroxide, with potassium *iso*cyanate or directly from β-iodopropionic acid, the latter method being the more convenient. By bromination at 100° in glacial acetic acid in a special apparatus, the bromodihydrouracil described by Fischer and Roeder (Abstr., 1901, i, 294) was obtained, crystallising in flat needles or plates, melting at 195°, and decomposing into uracil and hydrogen bromide at a slightly higher temperature. *Thiocyanodihydrouracil,* obtained from this by the action of potassium thiocyanate in alcohol, crystallises in needles melting at 202—203° to a brown liquid. By the action of fuming hydrochloric acid at 170°, it is converted into iso*cysteine hydrochloride*, $NH_2\cdot CH_2\cdot CH(SH)\cdot CO_2H,HCl$, melting and decomposing at 141°, which gives a brownish-black precipitate with copper sulphate, dissolving in excess to a characteristic purple solution. Iodine converts it into iso*cystine hydriodide*, $S_2[CH(CO_2H)\cdot CH_2\cdot NH_2]_2,HI$, which separates from water in glistening crystals melting and decomposing at 189°. iso*Cystine*,

$$S_2[CH(CO_2H)\cdot CH_2\cdot NH_2]_2,$$

sinters at 180° and melts to a reddish-brown mass at 185°; it gives a black coloration with cold alkaline lead solutions and a blackish-brown coloration with copper sulphate.

*iso*Cysteine hydrochloride is oxidised by bromine water to iso*cysteinic acid*, $NH_2\cdot CH_2\cdot CH(SO_3H)\cdot CO_2H$, crystallising in well-defined octahedra and pyramids which melt and decompose at 272—274°; it forms a well-defined blue copper salt.

Anilinodihydrouracil, $NHPh\cdot CH{<}{\begin{matrix}CH_2\cdot NH\\ CO{-}NH\end{matrix}}{>}CO$, formed by the interaction of bromodihydrouracil and aniline, crystallises in colourless, quadratic plates which sinter at 229° and melt and decompose at 239°. On heating it with hydrochloric acid at 170°, phenylethylenediamine, $NH_2\cdot CH_2\cdot CH_2\cdot NHPh$, is formed, melting at 199—200° and yielding a picrate melting at 179—180° (Abstr., 1889, 1166).

The formation of this diamine confirms the assumed formula of bromodihydrouracil. E. F. A.

Solubility and Heat of Solution of Carbamide. Energy Equilibrium. Otto Krummacher (*Zeit. biol.*, 1905, **28**, 302—321. Compare Rubner, *ibid.*, **20**, 414).—The specific heat of a 1·804 per cent. aqueous carbamide solution is 0·988; the heat of combustion of pure carbamide is 2·532 Cal. and the heat of solution 3·57 Cal. The numbers varied somewhat according to the calorimeter employed. With a small calorimeter, the mean value was 3·54, and with a large calorimeter 3·62. All possible precautions were taken. Previous determinations are: Rubner, 3·679; Berthelot and Petit, 3·580; J. Thomsen, 3·349; and Speyers, 3·628.

The solubility of carbamide in water at different temperatures has been determined. One gram of water dissolves 0·779 gram of carbamide at 5·5°, 1·000 at 17·1°, and 1·094 at 20·92°. The heat of solution has been calculated from the data to be 3·608 Cal. for 5·5° and 20·9°. J. J. S.

Oxaluramide. MARTIN SCHENCK (*Ber.*, 1905, **38**, 459—461).—In the preparation of oxaluramide (Rosing and Schischkoff, *Annalen*, 1858, **106**, 255; Strecker, *ibid.*, 1860, **113**, 47) it is essential that a large excess of ammonia should not be employed, as concentrated ammonium hydroxide converts the amide into carbamide and ammonium oxalate and oxamate. Oxaluramide is not readily decomposed by hot water, and when subjected to destructive distillation yields ammonia, water, cyanic acid, and probably cyanuric acid and biuret. J. J. S.

Attempted Synthesis of Uric Acid. HENRY J. H. FENTON (*Proc. Camb. Phil. Soc.*, 1905, **13**, 25—26).—Trihydroxyacrylic acid, the parent acid, which on condensation with carbamide would be expected to yield uric acid, is as yet unknown. On oxidation of dihydroxymaleic acid with ferric or mercuric salts, the semialdehyde of mesoxalic acid, $CHO\cdot CO\cdot CO_2H$, is obtained. On the assumption that the aldehyde hydrate of this might be tautomeric with trihydroxyacrylic acid, the author has condensed the semialdehyde with carbamide. When the condensation is carried out in aqueous solution, carbon dioxide is evolved and glycoluril is obtained corresponding with the formula

$$CO<\begin{matrix}NH\cdot CH\cdot NH\\ \vert\\ NH\cdot CH\cdot NH\end{matrix}>CO.$$

This is probably produced by the decomposition of glycolurilcarboxylic acid.

When glycoluril is evaporated to dryness on a water-bath with concentrated nitric acid and the residue treated with sodium hydroxide, a slight pink or orange colour is developed which, on addition of sodium hypochlorite, changes to an intense purple. H. M. D.

[Acetyl-lactonitrile. Acetylsalicylphenetidide.] Correction. RICHARD ANSCHÜTZ (*Ber.*, 1905, **38**, 719).—Acetyl-lactonitrile (Abstr., 1904, i, 966) and acetylsalicylphenetidide (*ibid.*, 990), which were described as new substances, had been prepared previously.

W. A. D.

Application to Nitriles of the Method of Direct Hydrogenation by Catalysis; Synthesis of Primary, Secondary, and Tertiary Amines. PAUL SABATIER and JEAN B. SENDERENS (*Compt. rend.*, 1905, **140**, 482—486).—Aliphatic nitriles are directly hydrogenated in the presence of reduced nickel at 180° to 220° to the corresponding primary amine according to the equation $C_nH_{2n+1}\cdot CN + 2H_2 = C_nH_{2n+1}CH_2\cdot NH_2$, which at the high temperature employed is partially converted into the corresponding secondary and tertiary amines and ammonia according to the equations $2NH_2\cdot CH_2\cdot C_nH_{2n+1} = NH_3 + NH(CH_2\cdot C_nH_{2n+1})_2$; $3NH_2\cdot CH_2\cdot C_nH_{2n+1} = 2NH_3 + N(CH_2\cdot C_nH_{2n+1})_3$ (compare Abstr., 1904, i, 305, 661); the final product, therefore, is a mixture of the three amines in which the secondary amine preponderates when the reaction is conducted at about 200°; thus, in the case of acetonitrile, diethylamine constituted 3/5ths of the mixed amines, whilst propionitrile yielded on reduction 1 part of propylamine, 8 to 9 parts of dipropylamine, and 2 parts of

tripropylamine. Hexonitrile (α-cyano-γ-methylbutane), on direct hydrogenation at 200—220°, yields (1) 5 parts of β-methylpentane boiling at 62°, formed by the complete reduction of the nitrile; (2) 8 parts of *α-amino-δ-methylpentane*, $CHMe_2\cdot[CH_2]_3\cdot NH_2$, a colourless liquid with a disagreeable odour, boiling at 125° under 762 mm. pressure, slightly soluble in water, turning blue litmus red, forming a soluble *hydrochloride*, and uniting directly with carbon dioxide to form a *carbonate* crystallising in small, white prisms; the *oxalate* crystallises in long, thin needles melting at 166°, slightly soluble in water, readily so in warm alcohol, and it reacts with phenylcarbimide to form *phenyl*iso*hexylcarbamide*, $NHPh\cdot CO\cdot NH\cdot C_6H_{13}$, which crystallises from alcohol in thin, white needles melting at 84°; (3) *di*iso*hexylamine*, $NH(C_3H_6\cdot CHMe_2)_2$, a colourless liquid with a disagreeable odour, boiling at 134° under 35 mm. pressure or 225° under 762 mm., having a sp. gr. 0·797 at 0°/0°, is strongly alkaline towards litmus, and forms an unstable crystalline *carbonate*, an *oxalate* crystallising from alcohol in pearly plates which decompose at 220°, and combines with phenylcarbimide to form *phenyldi*iso*hexylcarbamide*,

$$NHPh\cdot CO\cdot N(C_6H_{13})_2,$$

which crystallises from alcohol in voluminous, colourless prisms melting at 104°; (4) *tri*iso*hexylamine*, $N(C_5H_{10}Me)_3$, a yellow liquid with a disagreeable odour boiling at 178° under 35 mm. or at 283° under 762 mm. pressure, has a sp. gr. 0·807 at 0°/0°, and forms a crystalline *oxalate* melting and decomposing above 250°.

The aromatic nitriles are converted almost exclusively into the corresponding hydrocarbon and ammonia on direct hydrogenation in the presence of nickel at 200°; thus benzonitrile yielded toluene and ammonia. M. A. W

Trimercuriacetaldehyde. KARL A. HOFMANN (*Ber.*, 1905, **38**, 663. Compare Biltz, this vol., i, 165).—A claim for priority in reference to the aldehydic nature of the precipitate caused by acetylene in mercury chloride solutions (see also Abstr., 1899, i, 97). E. F. A.

Preparation of *cyclo*Hexene from *cyclo*Hexanol. LÉON BRUNEL (*Bull. Soc. chim.*, 1905, [iii], **33**, 270—271. Compare Abstr., 1903, i, 680, 695, and Zelinsky and Zelikoff, Abstr., 1902, i, 2).—When *cyclo*hexanol is treated with phosphoric oxide, zinc chloride, or potassium hydrogen sulphate, *cyclo*hexene is formed; the yield with zinc chloride varies from 65 to 70 per cent. and with potassium hydrogen sulphate from 82—83 per cent. of the theoretical, the loss in each case being due to the formation of condensation products. A description of the best method of carrying out the operation is given. T. A. H.

The Friedel and Crafts Reaction. JACOB BOESEKEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, **7**, 470—473. Compare Abstr., 1903, i, 617; 1904, i, 384).—A discussion of the mechanism of the Friedel-Crafts reaction. A. McK.

Action of Alkalis on Phenylnitroethylene. JAKOB MEISENHEIMER and FRIEDRICH HEIM (*Ber.*, 1905, 38, 466—473).—An ice-cold suspension of phenylnitroethylene in aqueous methyl alcohol readily reacts with a solution of sodium methoxide, yielding a clear solution containing presumably the compound OMe·CHPh·CH:NO·ONa, from which *β-nitro-α-methoxy-α-phenylethane*, $OMe\cdot CHPh\cdot CH_2\cdot NO_2$, can be obtained by means of carbon dioxide. It is a colourless oil and distils at 135—136° under 12 mm. pressure. It is not decomposed when the ethereal solution is boiled with concentrated hydrochloric acid, and the addition of mineral acids to solutions of its alkali salts yields phenylnitroethylene. *β-Nitro-α-ethoxy-α-phenylethane* distils at 136—137° under 12 mm. pressure.

β-Nitro-α-hydroxy-α-phenylethane cannot be obtained in a pure state by the action of carbon dioxide on an aqueous solution of its sodium derivative (Thiele and Haeckel, Abstr., 1903, i, 160).

βδ-Dinitro-α-methoxy-αγ-diphenylbutane,

$$OMe\cdot CHPh\cdot CH(NO_2)\cdot CHPh\cdot CH_2\cdot NO_2,$$

is formed when the alkaline solution, obtained in the preparation of nitromethoxyphenylethane, is kept for some 40 hours, and a current of carbon dioxide then passed through without the addition of water. The yield varies from 15—35 per cent. The product crystallises from methyl alcohol in large, colourless needles, melts at 151—152°, is only sparingly soluble in ether or cold methyl or ethyl alcohol, and does not readily reduce alkaline permanganate. Its alkaline solution reacts with benzenediazonium acetate solution (Bamberger, Abstr., 1899, i, 108), yielding a *monophenylhydrazone*, $C_{23}H_{22}O_5N_4$, melting and decomposing at 169—170°; the same compound is obtained even in the presence of excess of the diazonium solution. Bromine water reacts with an alkaline solution yielding a *tribromo*-derivative, $C_{17}H_{15}O_5N_2Br_3$, melting and decomposing at 182°.

Sodium and potassium salts have been obtained, for example, $C_{17}H_{16}O_5N_2Na_2,2MeOH$, but they are very unstable.

βδ-Dinitro-α-ethoxy-αγ-diphenylbutane crystallises in felted needles and melts at 156°. J. J. S.

Picrates and other Additive Products of Unsaturated Compounds. GIUSEPPE BRUNI and ERCOLE TORNANI (*Atti R. Accad. Lincei*, 1905, [v], 14, i, 154—157. Compare Abstr., 1904, i, 875).—Indene and *s*-trinitrobenzene yield an *additive compound*,

$$C_9H_8,C_6H_3(NO_2)_3,$$

which separates from ethereal solution in long, lemon-yellow needles melting at 101—102°.

With picryl chloride, indene gives an *additive compound*,

$$C_9H_8,C_6H_2Cl(NO_2)_3,$$

which crystallises from ether in long, lemon-yellow needles melting at 39°.

The *additive compound* of *iso*apiole and *s*-trinitrobenzene,

$$C_{18}H_{17}O_{10}N_3,$$

is deposited from alcohol in dark orange, silky, acicular crystals melting at 66—67°.

With picryl chloride, *iso*apiole gives an *additive compound*,

$$C_{18}H_{16}O_{10}N_3Cl,$$

which separates from alcohol in rose-red, acicular crystals melting at 55—56°.

*iso*Apiole from dill oil and *s*-trinitrobenzene yield an *additive compound*, $C_{18}H_{17}O_{10}N_3$, which crystallises from alcohol in shining, red needles melting at 76—77°.

Picryl chloride and *iso*apiole from dill oil form an *additive compound*, $C_{18}H_{16}O_{10}N_3Cl$, which separates from alcohol in red, acicular crystals melting at 43—44°.

*iso*Myristicin and picryl chloride give an *additive compound*,

$$C_{17}H_{14}O_9N_3Cl,$$

which crystallises from alcohol in dark red prisms melting at 65—66°.

Tolane picrate, $C_{14}H_{10},2C_6H_3O_7N_3$, crystallises from ether in pale yellow plates which melt at 111° and explode at a higher temperature.

Quinone picrate, $C_6H_4O_2,C_6H_7O_7N_3$, separates from ether in large, lemon-yellow crystals melting at 78—79°. T. H. P.

Melting Point Curve for Mixtures of Anthracene and Picric Acid. ROBERT KREMANN (*Monatsh.*, 1905, **26**, 143—148. Compare this vol., ii, 76, 77).—The melting point curve for mixtures of anthracene and picric acid falls from the melting point of anthracene to about 141°, where there is a break, and then to a eutectic point at about 106° for a mixture containing about 86 molecular per cent. of picric acid; the break at 141° represents the eutectic point between the molecular additive compound which melts at 152·5° (Behrend, Abstr., 1895, ii, 71) and anthracene. G. Y.

Syntheses in the Anthracene Series. IV. Tetra-alkyl Derivatives of 9 : 10-Diaminodiphenyl-9 : 10 diphenyldihydroanthracene. ALBIN HALLER and ALFRED GUYOT (*Compt. rend.*, 1905, **140**, 343—345. Compare Abstr., 1904, i, 314, 660, and this vol., i, 188).—9 : 10-Dihydroxy-9 : 10-diphenyldihydroanthracene readily condenses with dimethyl- or diethyl-aniline in acetic acid solution, and the product consists of equal quantities (45 per cent. of each) of the *cis*- and *trans*-stereoisomerides of the corresponding 9 : 10-tetra-alkyldiaminodiphenyl-9 : 10-diphenyldihydroanthracenes, which are readily separated by their difference in solubility and melting point. The first form, 9 : 10-*tetramethyldiaminodiphenyl*-9 : 10-*diphenyldihydroanthracene*, $C_{14}H_8Ph_2(C_6H_4{\cdot}NMe_2)_2$, forms small, brilliant prisms melting above 360° and almost insoluble in the ordinary solvents; the *platinichloride* forms thin, yellow needles; the second form is obtained in white crystals melting at 275°, more readily soluble than its isomeride; the *platinichloride* is slowly deposited from solution in golden leaflets. The two stereoisomerides of 9 : 10-*tetraethyldiaminodiphenyl*-9 : 10-*diphenyldihydroanthracene* are colourless, crystalline compounds melting at 250° and 230° respectively. M. A. W.

Structural Formula for Triphenylmethyl. ALEXEI E. TSCHITSCHIBABIN (*Ber.*, 1905, **38**, 771—773. Compare this vol., i, 125, and Jacobson, *ibid.*, 186).—Further arguments in favour of the

hexaphenylethane formula for Gomberg's triphenylmethyl are brought forward, but the question is not regarded as finally settled.

J. J. S.

Action of Ethyl *iso*Succinate on Aniline, *p*-Toluidine, and *p*-Aminophenol. EZIO COMANDUCCI and R. LOBELLO (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1905, [iiia], 11, 18—27).—The interaction of molecular proportions of aniline and ethyl *iso*succinate at 180° yields: (1) iso*succinodianilide*, $CHMe(CO{\cdot}NHPh)_2$, which crystallises from alcohol in shining, white, silky scales melting at 214° and dissolves in acetic acid and, to a slight extent, in chloroform or benzene; with concentrated nitric acid, it gives first a brown and then a green coloration, but with ferric chloride its alcoholic solution yields no coloration. (2) *Ethyl* iso*succinanilate*, $NPh\colon C(OH){\cdot}CHMe{\cdot}CO_2Et$, which separates from the mother liquor in microscopic, white crystals melting at 173—174° and soluble in the same solvents as the above compounds; with fuming nitric acid, it gives oily, reddish-brown drops, whilst with ferric chloride the alcoholic solution yields a brownish-red solution which changes to violet and later to grey on dilution with water. iso*Succinanilic acid*, $NPh\colon C(OH){\cdot}CHMe{\cdot}CO_2H$, forms a white, crystalline powder which begins to melt and decompose at 175° and melts into a red liquid at 180°.

The interaction of molecular proportions of *p*-toluidine and ethyl *iso*succinate at 180° yields: (1) iso*succinodi*-p-*toluidide*,

$$CHMe(CO{\cdot}NH{\cdot}C_6H_4Me)_2,$$

which crystallises from alcohol in slender, silky needles melting at 245° and dissolves in acetic acid and, to a slight extent, in chloroform or benzene; with fuming nitric acid, it gives an orange solution which deposits yellow flocks on the addition of water; its alcoholic solution gives no coloration with ferric chloride. (2) *Ethyl* iso*succino*-p-*toluidate*, $C_6H_4Me{\cdot}N\colon C(OH){\cdot}CHMe{\cdot}CO_2Et$, which crystallises from alcohol in large, transparent plates melting at 85—87° and dissolving in acetic acid, chloroform, or benzene; it is turned yellow by fuming nitric acid, and its alcoholic solution gives an intense reddish-violet coloration with ferric chloride. iso*Succino*-p-*toluidic acid*,

$$C_6H_4Me{\cdot}N\colon C(OH){\cdot}CHMe{\cdot}CO_2H,$$

separates in white needles, which melt and decompose at 145° and in alcoholic solution yields a pale red coloration with ferric chloride.

iso*Succinodi*-p-*hydroxyanilide*, $CHMe(CO{\cdot}NH{\cdot}C_6H_4{\cdot}OH)_2$, obtained from *p*-aminophenol and ethyl *iso*succinate, separates from benzene in dirty-white crystals melting at 136—137° and gives a yellow coloration with fuming nitric acid, but none with ferric chloride.

The interaction of molecular proportions of *p*-anisidine and ethyl *iso*succinate at 170—175° yields: (1) iso*succinodi*-p-*methoxyanilide*, $CHMe(CO{\cdot}NH{\cdot}C_6H_4{\cdot}OMe)_2$, which crystallises from alcohol in white needles melting at 200—201° and is soluble in acetic acid and, to a slight extent, in benzene or chloroform; with fuming nitric acid, it gives an orange liquid yielding a yellow, flocculent precipitate with water, whilst its alcoholic solution gives a faint green coloration with ferric chloride. (2) *Ethyl* iso*succino*-p-*methoxyanilamate*,

$$OMe{\cdot}C_6H_4{\cdot}N\colon C(OH){\cdot}CHMe{\cdot}CO_2Et,$$

which separates from alcohol in white crystals melting at 112—114° and behaves towards fuming nitric acid, ferric chloride, and organic solvents like the previous compound. iso*Succino*-p-*methoxyanilic acid*, $OMe\cdot C_6H_4\cdot N\colon C(OH)\cdot CHMe\cdot CO_2H$, is a white, crystalline compound melting and decomposing at 143° and is soluble in water or acetic acid, and slightly so in benzene or chloroform; in alcoholic solution, it gives a reddish-yellow coloration with ferric chloride.

The interaction of *p*-phenetidine and ethyl *iso*succinate in molecular proportions at 190—192° yields: (1) iso*succinodi*-p-*ethoxyanilide*, $CHMe(CO\cdot NH\cdot C_6H_4\cdot OEt)_2$, which crystallises from alcohol in shining, white needles melting at 210° and resembles the preceding diamides in its behaviour towards concentrated nitric acid, ferric chloride, and organic solvents. (2) *Ethyl* iso*succino*-p-*ethoxyanilate*,

$$OEt\cdot C_6H_4\cdot N\colon C(OH)\cdot CHMe\cdot CO_2Et,$$

which forms small, white needles melting at 125—126° to a violet liquid; in alcoholic solution, it gives a violet coloration; with ferric chloride and with concentrated nitric acid, it yields an orange solution from which water precipitates a yellow, flocculent nitro-derivative. iso-*Succino*-p-*ethoxyanilic acid*, $OEt\cdot C_6H_4\cdot N\colon C(OH)\cdot CHMe\cdot CO_2H$, forms silky, white crystals which melt at 146—148° and dissolve in alcohol or acetic acid and, to a slight extent, in benzene or chloroform; with ferric chloride, it gives a pale orange coloration. T. H. P.

Preparation of Pure *o*-Toluidine and a Method for Ascertaining its Purity. ARNOLD F. HOLLEMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, **7**, 395).—In order to estimate the amount of *p*-toluidine in admixture with *o*-toluidine, the solidifying point of the acetylated product was determined. The following figures for the solidifying point of a mixture of aceto-*o*- and -*p*-toluidides were obtained: 109·15°, 108·45°, 107·75°, 103·2°, and 100·8°, corresponding with 0, 1·12, 2·42, 9·58, and 13·6 per cent. of the para-compound.

Details are quoted to show how small amounts of *p*-toluidine and of aniline may be detected by means of the sodidifying point figures, the *o*-toluidine being mixed in one case with 2 per cent. of aniline and in another with 2 per cent. of *p*-toluidine. A. McK.

Benzylmalimides. ALBERT LADENBURG and WALTER HERZ (*J. pr. Chem.*, 1905, [ii], **71**, 152).—A reply to Lutz (this vol., i, 191).

G. Y.

Amide Formation between Optically Active Acids and Bases. The Optically Active α-Aminoethylbenzenes. WILLY MARCKWALD and R. METH (*Ber.*, 1905, **38**, 801—810).—The method of Marckwald and McKenzie (Abstr., 1899, ii, 733; 1900, i, 207; 1901, ii, 229) for resolving inactive substances into their optically active components has been applied by the authors to the resolution of an inactive acid by an active base and of an inactive base by an active acid.

When equal weights of *r*-mandelic acid and *l*-menthylamine are

heated together for 10 hours at 160—170°, the product is a mixture of menthylamine mandelate and mandelmenthylamide, which, when agitated with aqueous sodium hydroxide, yields sodium mandelate ; from this, a lævorotatory mandelic acid, having $[\alpha]_D -5\cdot1°$ $(c=12\cdot5)$ in aqueous solution, was prepared. *d*-Mandelic acid is accordingly more quickly converted into amide by *l*-methylamine than is *l*-mandelic acid. The ratio of the rate of amide formation between *l*- and *d*-mandelic acids respectively and *l*-menthylamine, calculated by the formula $c=(\log a - x/a)/(\log b - y/b)$, is $c=0\cdot862$.

That *d*-α-phenylethylamine undergoes amide formation with *l*-quinic acid more slowly than the *l*-base was proved by heating together equivalent weights of *i*-α-phenylethylamine and *l*-quinic acid for $4\frac{1}{2}$ hours at 165° and then recovering the residual base, which showed a marked dextrorotation. When this latter product was again submitted to fractional amide formation with *l*-quinic acid, the residual base had $\alpha_D + 3\cdot5°$ $(l=1)$.

The mixture of *l*-quinic acid-*l*-phenylethylamide and *l*-quinic acid-*d*-phenylethylamide formed contains an excess of the former, which is readily separated by crystallisation from water. l-*Quinic acid*-l-*phenylethylamide* melts at 220° and has $[\alpha]_D - 92\cdot1°$ $(c=6\cdot692)$ in pyridine solution. When boiled with fuming hydrochloric acid, it forms *i*-α-chloroethylbenzene and l-α-*phenylethylamine*, which has *d* 0·9503 at 22°/4° and $[\alpha]_D - 39\cdot51°$ at 22°. Its rotation dispersion was also examined. Its hydrochloride melts at 171° and has $[\alpha]_D - 3\cdot5°$ $(c=4)$ in aqueous solution (compare Kipping and Hunter, Trans., 1903, 83, 1147). No racemisation of the base had occurred during its formation from the amide.

The isolation of the *d*-base from the product, which had not been converted into amide during the fractional amide formation of the *i* base with *l*-quinic acid, was effected by aid of the fact that the sulphate of the *i*-base is a *dl*-conglomerate and not an *r*-compound (compare Abstr., 1899, i, 477). d-α-*Phenylethylamine sulphate* melts and decomposes at 272°. The free *base* has $[\alpha]_D + 39\cdot66°$; its *carbamide* melts at 122—123° and has $[\alpha]_D + 46\cdot2°$ $(c=4\cdot035)$. By the action of sodium nitrate on the *l*-sulphate, a dextrorotatory phenylmethylcarbinol, having $[\alpha]_D + 2\cdot7°$, was obtained, during the formation of which optical inversion may have occurred.

The *benzoyl* derivative of *l*-α-phenylethylamine melts at 125·5°. Although practically inactive in ethyl-alcoholic solution, complete racemisation does not occur during its preparation by the Schotten-Baumann method, as is supposed by Kipping and Hunter (*loc. cit.*). The authors have determined its specific rotation in benzene, chloroform, propyl alcohol, ethyl alcohol, and methyl alcohol respectively.

A. McK.

Benzylethylaniline. Robert Gnehm (*J. pr. Chem.*, 1905, [ii], 71, 150—151).—Contrary to Schultz, Rohde, and Bosch's suggestion (Abstr., 1904, i, 992), Gnehm and Scheutz (Abstr., 1901, i, 519) did not make an exhaustive investigation of the action of nitric acid on benzylethylaniline.

G. Y.

Benzylethylaniline and Benzylideneaniline. Wilhelm Vaubel and O. Scheuer (*Zeit. Farb. Text. Ind.*, 1905, **4**, 88—89).—On brominating benzylethylaniline dissolved in glacial acetic acid by means of potassium bromide, potassium bromate, and hydrochloric acid, benzyl bromide and ethylaniline are first formed, the latter subsequently undergoing conversion into tribromoethylaniline. Benzylideneaniline under similar treatment gives tribromoaniline. Both benzylethylaniline and benzylideneaniline possess very feebly basic properties; even when small quantities of acid are added to large quantities of the bases either suspended in water or dissolved in ether, there is practically no formation of a salt. W. A. D.

Reaction between Tertiary Amines and Organo-magnesium Compounds. Franz Sachs and Ludwig Sachs (*Ber.*, 1905, **38**, 1087—1088. Compare this vol., i, 190).—The discrepancies between the found and calculated molecular refractions for the tertiary amines, &c., recently described (this vol., ii, 190) disappear when Brühl's figures for C, H, &c., are employed instead of those given by Ostwald in calculating the theoretical values. E. F. A.

Lossen's Reaction. Ernst Mohr (*J. pr. Chem.*, 1905, [ii], **71**, 133—149. Compare Lossen, *Annalen*, 1875, **175**, 313; Thiele and Pickard, Abstr., 1900, i, 29).—When warmed on the water-bath with concentrated alkali hydroxide, dibenzhydroxamic acid yields benzhydroxamic and benzoic acids with traces of aniline; with 1 mol. of an alkali hydroxide in dilute aqueous solution, the hydrolysis leads to the formation of diphenylcarbamide, carbon dioxide, benzoic acid, and small quantities of aniline, whilst with an excess of alkali hydroxide in $0{\cdot}1N$-aqueous solution the amount of diphenylcarbamide formed decreases, and that of the aniline increases, until with 3 mols. of alkali hydroxide only traces of the carbamide are obtained. The reaction is accompanied by an odour of phenylcarbylamine, which disappears on acidification.

The excess of dilute alkali hydroxide prevents the formation of diphenylcarbamide by accelerating the hydrolysis of the phenylcarbimide, first formed. In aqueous solution at 0°, phenylcarbimide is slowly converted into diphenylcarbamide, only traces of aniline being found in the solution, but with dilute potassium hydroxide at 0° phenylcarbimide is rapidly hydrolysed into aniline and carbon dioxide.

The formation of aniline in warm dilute alkali hydroxide solution may be used as a test for dibenzhydroxamic acid. G. Y.

Ethers and Esters of *cyclo*Hexanol. Léon Brunel (*Bull. Soc. chim.*, 1905, [iii], **33**, 271—274. Compare Abstr., 1903, i, 695, and 1904, i, 158).—The methyl and ethyl ethers were prepared either by the action of the appropriate alkyl iodide on the sodium derivative of *cyclo*hexanol or by the reduction of the corresponding alkyl phenyl ethers.

cyclo*Hexanyl methyl ether* is a colourless, mobile liquid, which boils at 135·5°, has a sp. gr. 0·902 at 0°, and does not decolorise bromine or potassium permanganate. The *ethyl ether* resembles the foregoing, boils at 149·5°, has a sp. gr. 0·891 at 0°, and is slightly soluble in water, readily so in alcohol and ether.

cyclo*Hexanyl formate*, obtained by the action of formic acid on the alcohol, is a colourless, mobile liquid of agreeable odour; it boils at 162·5° and has a sp. gr. 1·010 at 0°. The *benzoate*, obtained by the action of benzoyl chloride on *cyclo*hexanol in presence of pyridine, is a colourless, mobile, inodorous liquid, which boils at 192—193° under 61 mm. pressure and has a sp. gr. 1·068 at 0°. cyclo*Hexanyl hydrogen succinate*, obtained by the action of succinic anhydride, alone and in excess, or in mol. proportion in presence of pyridine, on the alcohol, forms colourless crystals, melts at 44°, and is soluble in alcohol and ether. The normal *succinate*, obtained by the action of succinyl chloride on *cyclo*hexanol in presence of pyridine, is a colourless, inodorous syrup. cyclo*Hexanyl hydrogen phthalate* separates from alcohol in large crystals and melts at 99°. The normal *ester* forms large, prismatic, colourless crystals and melts at 66°. T. A. H.

The Three Methyl*cyclo*hexanones and the Corresponding Methyl*cyclo*hexanols. Paul Sabatier and Alphonse Mailhe (*Compt. rend.*, 1905, **140**, 350—352).—The three methyl*cyclo*hexanols are readily prepared by the direct hydrogenation of *o*-, *m*-, or *p*-cresol in the presence of reduced nickel at 200—220° (compare Sabatier and Senderens, Abstr., 1904, i, 156), and the ketones are obtained by the action of copper at 300° on the corresponding alcohols (compare Sabatier and Senderens, Abstr., 1903, i, 454; 1904, i, 156). 1 : 2-Methyl*cyclo*hexanol, a colourless liquid boiling at 164·5—165·5° under 745 mm. pressure, has a sp. gr. 0·9452 at 0°/0°, its acetyl derivative has a fruity odour, boils at 181·5—182·5° (corr.), and has a sp. gr. 0·968 at 0°/0°; its phenylcarbamate forms brilliant prisms melting at 105°; it yields two isomeric methyl*cyclo*hexenes on treatment with zinc chloride, one boiling at 108—109° and having a sp. gr. 0·823 at 0°/0°, the other boiling at 103—105° and having a sp. gr. 0·821 at 0°/0°. 1 : 2-Methyl*cyclo*hexanone is a colourless liquid boiling at 162—163° (corr.), has a sp. gr. 0·9441 at 0°/0°, and its semicarbazone melts at 191°.

1 : 3-Methyl*cyclo*hexanol is a colourless liquid boiling at 172·5° under 745 mm. pressure, has a sp. gr. 0·9336 at 0°/0°; its acetyl derivative boils at 185·5° (corr.) and has a sp. gr. 0·960 at 0°/0°; its phenylurethane forms large, thick crystals melting at 96° and on treatment with zinc chloride it yields a methyl*cyclo*hexene, boiling at 105° (corr.), and having a sp. gr. 0·819 at 0°/0° (compare Markownikoff, Abstr., 1900, i, 579).

1 : 3-Methyl*cyclo*hexanone is a colourless liquid, boiling at 169° under 765 mm. pressure, has a sp. gr. 0·9330 at 0°/0° and yields a semicarbazone, crystallising from methyl alcohol in rhombic plates melting at 182·5°.

1 : 4 *Methyl*cyclo*hexanol* is a colourless, viscous liquid boiling at 172·5—173° under 745 mm. pressure, has a sp. gr. 0·9328 at 0°/0°, forms a *phenylcarbamate* crystallising in brilliant prisms and melting at 125°, and on treatment with zinc chloride yields the same methyl*cyclo*hexene as that yielded under similar conditions by the 1 : 3-isomeride. 1 : 4-Methyl*cyclo*hexanone boils at 169·5°, has a sp. gr. 0·9332 at 0°/0°, and forms a semicarbazone which crystallises from alcohol in thick,

oblique prisms melting at 197° (compare Einhorn, Abstr., 1897, i, 345). M. A. W.

A New Method of Synthesising Alkyl Derivatives of Certain Saturated Cyclic Alcohols. Preparation of Homologues of Menthol. ALBIN HALLER and FRANÇOIS MARCH (*Compt. rend.*, 1905, **140**, 474—479).—Haller has already shown that camphor reacts with the sodium alkyloxides to form the corresponding alkyl derivative of camphor and of borneol (compare Abstr., 1892, 72), and an extension of the investigation to other cyclic ketones shows that methyl-3-*cyclo*hexanone reacts with the sodium alkyloxides at 220—225° in an autoclave to form the 1-methyl-4-alkyl-3-*cyclo*hexanol, 1 : 3-methyl*cyclo*hexanol, and the sodium salt of the acid corresponding with the alcohol employed, according to the equation :

$$2CH_2{<}{\begin{matrix}CHMe{\cdot}CH_2\\CH_2{-}{-}CH_2\end{matrix}}{>}CO + RCH_2{\cdot}ONa + RCH_2OH =$$

$$CH_2{<}{\begin{matrix}CHMe{-}{-}{-}{-}CH_2\\CH_2{\cdot}CH(CH_2R)\end{matrix}}{>}CH{\cdot}OH +$$

$$CH_2{<}{\begin{matrix}CHMe{\cdot}CH_2\\CH_2{-}{-}CH_2\end{matrix}}{>}CH{\cdot}OH + RCO_2Na.$$

The phenols thus obtained were identical with those prepared by reducing the corresponding 1-methyl-4-alkyl-3 *cyclo*hexanones (compare this vol., i, 214). 1-Methyl-4-propyl-3-*cyclo*hexanol boils at 111—113° under 23 mm. pressure, has a sp. gr. 0·9105 at 0°/4° or 0·8976 at 19°/4°, $[\alpha]_D - 18°$ at 19°, and forms a *phenylcarbamate*, which crystallises in long, thin needles melting at 108—109°. 1-Methyl-4-*iso*butyl-3-*cyclo*hexanol, melting at 68—69°, has $[\alpha]_D - 70°22'$, and forms a crystalline *phenylcarbamate* melting at 77° ; the liquid stereoisomeride, boiling at 110—111° under 16 mm. pressure, has $[\alpha]_D - 18°8'$ to $- 22°11'$. 1-*Methyl*-4-iso*amyl*-3-cyclo*hexanol* boils at 137° under 23—24 mm. pressure, has a sp. gr. 0·9000 at 0°/4° or 0·8909 at 20°/4°, and $[\alpha]_D - 24°28'$, and does not form a crystalline phenylcarbamate. M. A. W.

4-Benzyl-1-methyl-3-*cyclo*hexanol and 2 : 4-Dibenzyl-1-methyl-3-*cyclo*hexanol. ALBIN HALLER and FRANÇOIS MARCH (*Compt. rend.*, 1905, **140**, 624—629).—When 1-methyl-3-*cyclo*hexanone is heated at 220—225° for 24 hours with benzyl alcohol in which sodium has been dissolved, a mixture of 4-benzyl-1-methyl-3-*cyclo*hexanol and 2 : 4-dibenzyl-1-methyl-3-*cyclo*hexanol is obtained. On distillation under 21 mm. pressure, a considerable fraction can be collected between 180° and 187° and a second fraction between 240° and 265°.

From the first fraction, two products are obtained, both of which correspond with the formula $C_{14}H_{20}O$. The first melts at 101·5—102° and has $[\alpha]_D - 53°21'$ in absolute alcohol. The second melts at 79—80°. The two substances are in all probability stereoisomeric forms of 4-benzyl-1-methyl-3-*cyclo*hexanol. The first of these is identical with the substance obtained by Wallach (Abstr., 1897, i, 159) by reduction of 4-benzylidene-1-methyl-3-*cyclo*hexanone by means of

sodium ethoxide in ethyl alcohol. It is also obtained by boiling 1-methyl-3-*cyclo*hexanol with sodium in presence of toluene and adding benzaldehyde in small portions at a time to the boiling mixture.

On redistillation, the main portion of the second fraction passes over at 257—258°. The product thus obtained is 2 : 4-dibenzyl-1-methyl-3-*cyclo*hexanol and has $[\alpha]_D - 10°5'$ in absolute alcohol.

The results indicate that methyl*cyclo*hexanone behaves differently from camphor when reduced at high temperatures with sodium in benzyl alcohol solution. In the case of camphor, the only action is one of substitution, but with methyl*cyclo*hexanone reduction also takes place. H. M. D.

Tribromophenol Bromide: its Detection, Estimation, Rate of Formation, and Reaction with Hydriodic Acid. S. J. Lloyd (*J. Amer. Chem. Soc.*, 1905, **27**, 7—15).—Ammonia and many organic bases react with tribromophenol bromide with formation of coloured substances. These reactions are of value for the detection of the compound. When a solution of aniline or benzidine in chloroform is added to a solution containing tribromophenol bromide, a coloration is produced which is deep red in the case of the former reagent and intense green (or purple if concentrated) in the case of the latter.

The estimation of tribromophenol bromide may be effected by reducing the compound with zinc dust and sulphuric acid and determining the amount of hydrogen bromide formed.

The formation of tribromophenol bromide when phenol is treated with bromine water is due to the gradual action of the excess of bromine water on the tribromophenol which is first produced. Experiments were made to determine the amount of tribromophenol bromide formed when bromine reacts with phenol under varying conditions. It is found that the amount of tribromophenol bromide produced increases with the time during which the bromine is left in contact with the tribromophenol, although under ordinary conditions a considerable quantity may be formed in a few minutes. The results also show that in order to avoid the formation of tribromophenol bromide in the titration of phenol with bromine, the liquid must be strongly acid or must contain an excess of potassium bromide; a large excess of bromine must not be employed, and the precipitated tribromophenol must not be left too long with the excess of bromine water. Since the rate of formation of tribromophenol bromide is decreased by the addition of acid or potassium bromide, and increased by adding water or bromine or by raising the temperature, the conclusion is drawn that the action is due to the presence of hypobromous acid in the bromine water.

Tribromophenol bromide is not reduced quantitatively to tribromophenol by hydriodic acid under ordinary conditions, but is partially converted into other products. E. G.

Trinitroveratrole. Jan J. Blanksma (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, **7**, 462—465).—When 3 : 5-dinitroveratrole is nitrated, the nitro-group is introduced between the two existing nitro-groups; the trinitroveratrole formed is thus 3 : 4 : 5-nitro-1 : 2-di-

methoxybenzene, and is identical with the substance formed by the nitration of 3 : 5-dinitrocatechol dimethyl ether.

By interaction of alcoholic ammonia and trinitroveratrole, ammonium nitrite is formed together with 3 : 5-dinitro-2 : 4-diamino-1-methoxybenzene, which melts at 247° and is identical with the compound formed by the action of alcoholic ammonia on trinitroquinol dimethyl ether. When trinitroquinol dimethyl ether is treated with sodium methoxide, 3 : 5-dinitro-1 : 2 : 4-trimethoxybenzene, melting at 92°, is produced, and this, when treated with alcoholic ammonia, gives the same dinitrodiaminoanisole as was obtained from trinitroquinol dimethyl ether. The behaviour of trinitroveratrole with sodium methoxide is different, yellow crystals of a *compound* melting at 152°, and not affected by alcoholic ammonia, being obtained. A. McK.

Benzylphenyl Salicylate. VINCENZO MAJONE (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1904, [iiia], **10**, 393—394).—*Benzylphenyl salicylate*, $C_7H_5O_2{\cdot}O{\cdot}C_6H_4{\cdot}CH_2Ph$, obtained by the interaction of benzylphenol and salicylic acid in benzene solution in presence of phosphoric oxide, separates from alcohol in crystals melting at 90—91°, and dissolves in chloroform, acetone, benzene, or ether, and to a slight extent in light petroleum. T. H. P.

Action of Organo-magnesium Compounds on Doubly Unsaturated Ketones. HUGO BAUER (*Ber.*, 1905, **38**, 688—690).—*αεζ-Triphenyl-$\Delta^{\alpha\gamma}$-hexadiene-ε-ol*, $CHPh{:}CH{\cdot}CH{:}CH{\cdot}CPh(OH){\cdot}CH_2Ph$, prepared from cinnamylideneacetophenone and magnesium benzyl chloride, forms colourless needles and melts at 124—125°. *αε-Diphenyl-$\Delta^{\alpha\gamma}$-heptadiene-ε-ol*, $CHPh{:}CH{\cdot}CH{:}CH{\cdot}CPh(OH){\cdot}CH_2{\cdot}CH_3$, obtained from cinnamylideneacetophenone and magnesium ethyl iodide, crystallises from alcohol in colourless needles and melts at 76°. *αζ-Diphenyl-ε-methyl-$\Delta^{\alpha\gamma\epsilon}$-hexatriene*, $CHPh{:}CH{\cdot}CH{:}CH{\cdot}CMe{:}CHPh$, formed by the interaction of less than 1 mol. of cinnamylideneacetone with 1 mol. of magnesium benzyl chloride in ethereal solution, crystallises from alcohol in fluorescent leaflets and melts at 115—116°.

W. A. D.

Decahydro-β-naphthol and Octahydronaphthalene. HENRI LEROUX (*Compt. rend.*, 1905, **140**, 590—591. Compare Abstr., 1904, i, 986).—Decahydro-β-naphthol, $C_{10}H_{17}{\cdot}OH$, obtained by repeated hydrogenation of β-naphthol below 200°, crystallises from petroleum in colourless needles melting at 75°, boils at 115° under 13 mm. pressure, or at 230° with decomposition under the ordinary pressure, is slightly soluble in water, readily so in alcohol, benzene, ether, or carbon bisulphide, and is volatile in steam; the *acetyl* derivative, $C_{10}H_{17}{\cdot}OAc$, obtained by the prolonged action of acetic anhydride at 130°, is a colourless liquid with a fruity odour, boiling at 120° under 12 mm. or at 250° under the ordinary pressure; the *phenylcarbamate*, $NHPh{\cdot}CO{\cdot}OC_{10}H_{17}$, crystallises from light petroleum in thin, white needles melting at 165° and subliming at 160°. *Octahydronaphthalene*, $C_{10}H_{16}$, obtained when decahydro-β-naphthol is heated with potassium hydrogen sulphate, is a

liquid boiling at 190° (corr.) and having a sp. gr. 0·910 to 0·9009 at 13°; it unites directly with bromine to form *dibromo-octahydronaphthalene*, $C_{10}H_{16}Br_2$, which crystallises from alcohol in small, colourless prisms melting at 85°, readily soluble in chloroform, ether, or petroleum, and less so in alcohol or acetone. M. A. W.

Unsaturated Compounds. II. Addition of Mercaptans to Unsaturated Hydrocarbons. THEODOR POSNER [with J. S. TSCHARNO] (*Ber.*, 1905, **38**, 646—657).—Sulphides or sulphones could not be obtained from ethylene or propylene or from stilbene or diphenylbutadiene; trimethylethylene and amylene react with thiophenol or benzyl mercaptan, but not with ethyl mercaptan. *Phenyl-αβ-dimethylpropylsulphone*, $CHMe_2{\cdot}CHMe{\cdot}SO_2Ph$, prepared from trimethylethylene and thiophenol, crystallises in colourless plates melting at 32°; dimethylethylcarbinol bromide and sodium benzylsulphinate react forming the isomeric *phenyl-αα-dimethylpropylsulphone*, $CMe_2Et{\cdot}SO_2Ph$, which separates in colourless prisms melting at 70°. *Benzyl-αβ-dimethylpropylsulphone*, $CHMe_2{\cdot}CHMe{\cdot}SO_2{\cdot}C_7H_7$, forms needles melting at 58—59°.

Phenyl-β-phenylethylsulphone, $CH_2Ph{\cdot}CH_2{\cdot}SO_2Ph$, prepared from styrene and thiophenol, forms colourless plates which melt at 58°; the isomeric *phenyl-α-methylbenzylsulphone*, $CHPhMe{\cdot}SO_2Ph$, crystallises in colourless cubes melting at 115°. *Phenyl-β-phenylpropylsulphone*,

$$CHPhMe{\cdot}CH_2{\cdot}SO_2Ph,$$

separates in colourless plates melting at 94°; *benzyl-β-phenylpropylsulphone*, $CHPhMe{\cdot}CH_2{\cdot}SO_2{\cdot}CH_2Ph$, forms plates melting at 163°.

From pinene and benzyl mercaptan, as also from sabinene and thiophenol, only oils were obtained; camphene and benzyl mercaptan yielded *dihydrocamphene-β-benzylsulphone*, $C_7H_{12}{<}\begin{matrix}CH_2\\|\\CH{\cdot}CH_2{\cdot}SO_2{\cdot}C_7H_7\end{matrix}$, which separates from alcohol in plates melting at 127°; the corresponding *dihydrocamphene-β-phenylsulphone*, $C_7H_{12}{<}\begin{matrix}CH_2\\|\\CH{\cdot}CH_2{\cdot}SO_2Ph\end{matrix}$, crystallises in plates and melts at 73°. The isomeric *dihydrocamphene-α-phenylsulphone*, $C_7H_{12}{<}\begin{matrix}CH_2\\|\\CMe{\cdot}SO_2Ph\end{matrix}$, melts at 75°, whilst a mixture of the α- and β-derivatives melts at 60°.

Tetrahydronaphthalenephenylsulphone, $C_6H_6{<}\begin{matrix}CH_2{\cdot}CH_2\\|\\CH_2{\cdot}CH{\cdot}SO_2Ph\end{matrix}$, separates from alcohol in plates and melts at 139°; *dihydromenthenephenylsulphone*, $C_6H_9MePr^{\beta}{\cdot}SO_2Ph$, was obtained and analysed as a yellow oil. *Phenyl-δ-phenylbutenylsulphone*, $CHPh{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}SO_2Ph$, melts at 111°. cyclo*Pentanediphenyldisulphone*, $C_5H_8(SO_2Ph)_2$, was obtained in the form of colourless needles melting at 232—233°. From terpinene, terpinolene, sylvestrene or cedrene and thiophenol, oils were obtained corresponding in composition with additive products containing one molecule of the mercaptan. Crystallised acetates could not be prepared from these. *Tetrahydrolimonenediphenyldisulphone* crystallises in needles which melt and decompose at 236—237°. E. F. A.

The Ring System of Benzene. VII. HUGO KAUFFMANN and ALFRED BEISSWENGER (*Ber.*, 1905, **38**, 789—793. Compare Abstr., 1900, i, 480; 1901, i, 318; 1903, i, 19; 1904, i, 690).—It has already been shown that the carbethoxyl group acts as a fluorogen, and it is now shown that the acetyl and vinyl groups act in the same manner when introduced into the molecule of quinol dimethyl ether.

2 : 5-Dimethoxyacetophenone (Klages, Abstr., 1904, i, 1003) forms prismatic crystals melting at 20—22°, and in alcoholic solutions exhibits strong fluorescence. The *phenylhydrazone*, $C_{16}H_{18}O_2N_2$, crystallises in yellow prisms, melts at 99—100°, and is not stable in contact with the air; it does not fluoresce. A by-product melting at 50—51° and probably the monomethyl ether of quinacetophenone is obtained in the preparation of the dimethoxy-compound.

2 : 5-Dimethoxy-1-α-methylvinylbenzene (Klages, Abstr., 1904, i, 1004) may be obtained by distilling the corresponding carbinol under atmospheric pressure. Its vapour luminesces under the influence of Tesla rays, and its alcoholic solutions are fluorescent.

The quinol dimethyl ether and its two derivatives have anomalous molecular refractions. The two derivatives do not fluoresce in associating solvents. In methyl or ethyl alcohol, they possess only a feeble violet fluorescence, in *iso*butyl alcohol the fluorescence is most pronounced, and in benzyl alcohol the fluorescence is marked, but of a bluer shade. The temperature-coefficient of the fluorescence is also very considerable.

2 : 5-*Dimethoxy*-1-*αβ-dimethylvinylbenzene*, $C_6H_3(OMe)_3\cdot CMe\colon CHMe$, boiling at 254—255°, and dimethoxy-α-methylstilbene are also fluorescent. J. J. S.

The Ring System of Benzene. VIII. HUGO KAUFFMANN and AD. GROMBACH (*Ber.*, 1905, **38**, 794—801. Compare preceding abstract).—Benzoyl and other substituents have been introduced into the molecule of quinol dimethyl ether and the products investigated as regards their luminescence in presence of radium bromide, and also as regards their fluorescence. The following summary is given, where a = no. of cm. between the substance and 5 mg. of radium bromide when luminescence is just visible, b = distance when a sheet of zinc foil 0·75 mm. thick is interposed, and X = the substituent.

Quinol dimethyl ether, $a = 9{\cdot}3$, $b = 1{\cdot}0$; X = CPh(OH)(CH_2Ph), $a = 6{\cdot}5$, $b = 0{\cdot}3$; X = COPh, $a = 11{\cdot}7$, $b = 1{\cdot}0$; X = CEtPh·OH, $a = 13{\cdot}0$, $b = 1{\cdot}6$; X = CPhN⁚NHPh, $a = 13{\cdot}0$, $b = 1{\cdot}5$; X = CPh⁚CHPh, $a > 13{\cdot}0$, $b = 4{\cdot}9$; X = CPh_2·OH, $a > 13{\cdot}0$, $b = 5{\cdot}4$.

None of the compounds fluoresces, and it is obvious that substituents which increase the luminescence to an enormous degree need not necessarily function as "fluorogens."

Benzoylquinol dimethyl ether (2 : 5-*methoxybenzophenone*),

$$C_6H_3(OMe)_2\cdot COPh,$$

obtained by the Friedel-Craft synthesis, crystallises from light petroleum in pale yellow crystals, melts at 51°, distils at 225° under 30 mm. pressure, is readily soluble in most organic solvents, and is coloured a reddish-brown by concentrated sulphuric acid. The *phenylhydrazone* melts at 125°, the *monomethyl ether*, $OH\cdot C_6H_3(OMe)\cdot COPh$, melts at 78°.

Phenyl-2 : 5-*dimethoxyphenylethylcarbinol*, $C_6H_3(OMe)_2\cdot CEtPh\cdot OH$, obtained by the Grignard synthesis, forms large, clear crystals, melts at 56°, boils at 230° under 30 mm. pressure, and is readily soluble in the usual organic solvents with the exception of alcohol and light petroleum. With concentrated sulphuric or syrupy phosphoric acid, it gives a dark blue coloration.

α-Phenyl-α-2 : 5-*dimethoxyphenylpropylene*, $C_6H_3(OMe)_2\cdot CPh\colon CHMe$, obtained by the action of hydrogen chloride on the carbinol and subsequent distillation, is a colourless liquid distilling at 198° under 12 mm. pressure. It forms an unstable *dibromide*, which readily loses hydrogen bromide yielding the *β-bromo*-derivative,

$$C_6H_3(OMe)_2\cdot CPh\colon CBrMe.$$

Phenylbenzyl-2 : 5-*dimethoxyphenylcarbinol*,

$$C_6H_3(OMe)_2\cdot CPh(CH_2Ph)\cdot OH,$$

crystallises in long, colourless needles, melts at 110°, and is readily soluble in carbon disulphide, chloroform, or benzene.

2 : 5-*Dimethoxy-α-phenylstilbene*, $C_6H_3(OMe)_2\cdot CPh\colon CHPh$, obtained from the carbinol by means of hydrogen chloride, crystallises from light petroleum in large prisms melting at 82·5°; it yields an unstable oily *dibromide*, which readily loses hydrogen bromide, yielding a *monobromo*-derivative, $C_{22}H_{19}O_2Br$, melting at 118°.

Diphenyl-2 : 5-*dimethoxyphenylcarbinol*, $C_6H_3(OMe)_2\cdot CPh_2\cdot OH$, melts at 141° and is only sparingly soluble in alcohol or light petroleum.

J. J. S.

Dibenzylideneacetone and Triphenylmethane. VII. Adolf von Baeyer (*Ber.*, 1905, **38**, 569—590. Compare Abstr., 1902, i, 380, 769; 1903, i, 811; 1904, i, 308, 786, 898).—The halogen derivatives of triphenylcarbinol have been examined in order to prove that they do not possess the quinonoid structure. It had already been shown by Baeyer and Villiger that certain coloured derivatives of triphenylcarbinol cannot be represented as having this structure.

p-Trichloro- and *p*-tri-iodo-triphenylcarbinol form with concentrated sulphuric acid coloured salts, which, in contact with silver acetate, do not form silver chloride, as they would do if they were quinonoid in structure. The chromophore group in those salts is accordingly identical with that of triphenylcarbinol, the halogen atoms acting as auxochrome groups.

The basic properties of carbon are discussed. Carbon differs from other elements, which form "onium" bases, in that it forms salts only, the free base either not existing at all or being very unstable. The basic properties of carbon are shown in the coloured salts of triphenylmethyl. From the experiments of Walden and of Gomberg, who have shown that colourless derivatives of triphenylmethyl form a yellow solution with strongly dissociated solvents and that such solutions conduct electricity, the conclusion is drawn that one and the same compound can exist in two forms, a colourless one, which does not undergo electrolytic dissociation, and a coloured one, which does. The possibility of the existence of two triphenylcarbinols having the same composition and the same structural formula, but one of them being a strong coloured base and the other an indifferent colourless substance, is considered, as also is the possibility of existence of two

rosanilines, one coloured and basic and the other colourless and indifferent.

The distinction is drawn between an ionisable and a non-ionisable valency; the former is termed a "carbonium valency" and is indicated by a waved line, thus: $CPh_3{\cdot}OH + H_2SO_4 = Ph_3C \cdots\cdots O{\cdot}SO_3H + H_2O$.

The carbonium isomerism of phthaleins is discussed. The author does not consider that Werner's carboxonium salts contain quadrivalent oxygen, as supposed by Werner; they are regarded as carbonium salts, corresponding with the salts of triphenylmethyl. Thus the salt formulated by Werner as $C_6H_4{<}^{CH-}_{OBr}{>}C_6H_4$ is formulated by the author as $C_6H_4{<}^{CH}_{-O-}{>}C_6H_4\ Br$.

The colour in fulvene derivatives, in fuchsone and fuchsoneimine, and in aurin is due to the double linking, which is designated as a "carbonium double linking."

The paper also includes a discussion of triphenylmethyl derivatives which contain nitrogen; the formation of magenta from rosaniline; the action of alkali on magenta and on crystal-violet; the constitution of Homolka's base (diaminofuchsoneimine) and of dibenzylideneacetone, and the nature of azonium compounds.

p-*Trichlorotriphenylcarbinol*, prepared from *p*-chloroiodobenzene and methyl *p*-chlorobenzoate by means of Grignard's reaction, separates from light petroleum in needles or prisms and melts at 98—99°. It differs from triphenylcarbinol by being less basic, by the redder colour of its solutions and by the greater ease with which its sulphate crystallises. The *sulphate* forms brown, metallic prisms, which are immediately decomposed by water. When silver acetate is added to a solution of the sulphate in glacial acetic acid, silver chloride is not produced. When trichlorotriphenylcarbinol is warmed with a mixture of aniline hydrochloride and aniline, and the aniline then expelled by addition of sodium hydroxide and distillation in steam, the addition of picric acid to the benzene solution of the product gives the reaction characteristic of triphenylrosaniline.

p-*Trichlorotriphenylmethyl chloride*, $C_{19}H_{12}Cl_3{\cdot}Cl$, prepared by the action of acetyl chloride on *p*-trichlorotriphenylcarbinol, separates from light petroleum in glistening, colourless needles and melts at 113°. The *stannichloride* forms red crystals resembling chromic acid.

p-*Tri-iodotriphenylcarbinol*, prepared by the replacement of the three amino-groups in pararosaniline by iodine by Knoevenagel's method, separates from methyl alcohol in needles or prisms containing methyl alcohol of crystallisation, and from a mixture of ether and formic acid in colourless, quadratic plates, and melts at 162—163°. Its *sulphate* forms glistening, green crystals and does not yield silver iodide when acted on by silver nitrate.

p-*Tri-iodotriphenylmethyl chloride* separates from a mixture of light petroleum and chloroform in glistening prisms and melts and decomposes at 180°. A. McK.

Anethoglycol [γ-*p*-Methoxyphenylpropane-βγ-diol]. EUGÈNE VARENNE and L. GODEFROY (*Compt. rend.*, 1905, **140**, 591—593).—The

glycol of anethol (γ-p-*methoxyphenylpropane-βγ-diol*),

$$OMe{\cdot}C_6H_4{\cdot}CH(OH){\cdot}CHMe{\cdot}OH,$$

prepared by the action of alcoholic potassium hydroxide on dibromoanethole at the ordinary temperature, is a viscid, amber-coloured liquid possessing an aromatic and a sweet taste, having a sp. gr. 1·013 at 17° and boiling at 245—250°. The *monoacetate* is obtained by the action of acetic and hydrochloric acids on the glycol, and the *diacetate* by the action of acetyl chloride. M. A. W.

New Syntheses [of Esters] with Magnesium Organo-compounds. ALEXEI E. TSCHITSCHIBABIN (*Ber.*, 1905, **38**, 561—566).—The author describes several new applications of Grignard's reaction. When magnesium alkyl haloids act on normal carbonic esters, the main reaction is represented by the equation $RMgX + CO(OEt)_2 = R{\cdot}C(OMgX)(OEt)_2$. By the action of water on the compound obtained, an ester is formed, thus: $R{\cdot}C(OMgX)(OEt)_2 + H_2O = R{\cdot}CO_2Et + EtOH + MgX{\cdot}OH$. The yield of ester by this method is sometimes as much as 80 per cent. of the theoretical, whilst tertiary alcohols are formed to a very slight extent only.

Ethyl benzoate was prepared by the action of magnesium phenyl bromide on ethyl carbonate, ethyl *iso*hexoate by the action of magnesium *iso*amyl bromide on ethyl carbonate, and ethyl hexahydrobenzoate by the action of magnesium *cyclo*hexyl chloride on ethyl carbonate. The action of magnesium on the alkyl haloids was conducted in each case in an atmosphere of hydrogen.

If the reaction between magnesium organo-compounds and orthocarbonic esters be moderated and not too prolonged, it proceeds thus: $C(OEt)_4 + R{\cdot}MgX = R{\cdot}C(OEt)_3 + MgX(OEt)$. Tertiary alcohols are, however, formed in small amounts.

Ethyl orthobenzoate, prepared by the action of magnesium phenyl bromide on ethyl orthocarbonate, boils at 238—240° under 747 mm. pressure (Limpricht gives 220—225°), and has a sp. gr. 0·9902 at 20°/0°.

Ethyl orthopropionate, formed by the action of magnesium ethyl iodide on ethyl orthocarbonate, was not separated from the product of the reaction owing to the proximity of its boiling point with that of ethyl orthocarbonate. When the reaction was allowed to proceed vigorously, three fractions were obtained, the first containing ethyl propionate, the second ethyl orthopropionate, and the third *ethyl propionylpropionate acetal* [*ββ-diethoxy-α-methylvalerate*],

$$CH_2Me{\cdot}C(OEt)_2{\cdot}CHMe{\cdot}CO_2Et,$$

which boils at 223—226°. A 5 per cent. solution of hydrogen chloride converts it into ethyl propionylpropionate, from which diethyl ketone is prepared by hydrolysis with alkali. A. McK.

Condensation of Benzyl Chloride with the Aminobenzoic Acids. GIUSEPPE KERNOT and E. PETRONE (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1904, [iiia], **10**, 382—392).—Condensation of benzyl chloride with anthranilic acid in 96 per cent. alcoholic solution in presence of zinc yields the benzylanthranilic acid obtained by Henze (Abstr., 1899, i, 218). The *phenyl* ester, $C_7H_7{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2Ph$, separates from alcohol in tufts of pale yellow, prismatic crystals melt-

ing at 74—75°; the p-*tolyl* ester, $C_7H_7 \cdot NH \cdot C_6H_4 \cdot CO_2 \cdot C_6H_4Me$, forms prismatic needles melting at 79—80°, the m-*tolyl* ester, tufts of colourless, prismatic crystals which turn yellow on exposure to light, and the o-*tolyl* ester, minute crystals; the *β-naphthyl* ester forms mammillary masses of minute, white or pale yellow needles melting at 91—92°, and the *α-naphthyl* ester crystals melting at 76—77°.

Benzylanthranil, $C_6H_4<\begin{matrix} N \cdot C_7H_7 \\ | \\ CO \end{matrix}$, prepared by the action of phosphorus oxychloride on benzylanthranilic acid in toluene solution, crystallises from alcohol in tufts of monoclinic prisms [$a:b:c$ = 1·2695 : 1 : 1·0337; β = 57°29′], melting at 153·5—154°, and is soluble in the ordinary organic solvents.

The constitution of anthranil and its derivatives is discussed.

T. H. P.

Syntheses of Arylnitromethanes and of Stilbene Derivatives. WILHELM WISLICENUS and HENRY WREN (*Ber.*, 1905, **38**, 502—510).—The reactions previously described for the preparation of phenyl*iso*nitromethane and of stilbene (Abstr., 1902, i, 541) are now shown to be of general application.

o-Tolylacetonitrile (Abstr., 1885, 889), sodium ethoxide, and ethyl nitrate yield *sodium* o-*tolyl*iso*nitroacetonitrile*, $C_6H_4Me \cdot C(CN){:}NO \cdot ONa$, which dissolves in water to a colourless, neutral solution; when acidified at 0°, it yields the tolyl*iso*nitroacetonitrile as a white precipitate, which gives a red coloration with ferric chloride. It is extremely unstable and is readily transformed into a red resin.

o-Tolylnitromethane, $C_6H_4Me \cdot CH_2 \cdot NO_2$ (Goldberg, Abstr., 1901, i, 33), is obtained when the sodium derivative is boiled for some time with aqueous sodium hydroxide, but when more concentrated alkali and a higher temperature (200°) are employed a good yield of o-*dimethylstilbene* is obtained. This crystallises from methyl alcohol in flat, colourless needles melting at 82·5—83°. The *picrate* forms red needles melting at 102—103°.

Sodium m-*tolyl*iso*nitroacetonitrile* crystallises readily from absolute alcohol, and with alkali yields *m*-tolylnitromethane (Heilmann, Abstr., 1891, 201) or m-*dimethylstilbene*, the *picrate* of which melts at 96·5—97·5°. The *p*-dimethylstilbene has been prepared in a similar manner.

α-Naphthylmethyl chloride (Scherler, Abstr., 1892, 493) is best prepared by leading chlorine into *α*-methylnaphthalene at 250° until the increase in weight is 50 per cent. of the theoretical, and subsequent fractionation. The corresponding *nitrile* is an oil distilling at 191—194°. Sodium *α*-naphthyl*iso*nitroacetonitrile appears to have the composition $C_{10}H_7 \cdot C(CN){:}NO \cdot ONa,H_2O$. When boiled with dilute sodium hydroxide and acidified, it yields *α-naphthylnitroacetamide*, $C_{10}H_7 \cdot CH(NO_2) \cdot CO \cdot NH_2$, melting at 155—156°. With more concentrated alkali, it yields *α-naphthylnitromethane*, which crystallises from light petroleum in yellow needles melting at 72—73°. With sodium hydroxide at 150—160°, *α*-dinaphthastilbene (Elbs, Abstr., 1893, i, 271) is formed.

β-Naphthylnitromethane dissolves readily in all organic solvents and melts at about 72°. *β-Dinaphthastilbene* crystallises from benzene in colourless plates melting at 254—255°.

The nitro-compounds give Gabriel's reaction. J. J. S.

Elimination of Carbon Monoxide from Tertiary Acids with Concentrated Sulphuric Acid. II. Augustin Bistrzycki and Eugen Reintke (*Ber.*, 1905, 38, 839—848).—*αα*-Ditolylpropionic acid, when shaken in the cold with concentrated sulphuric acid, loses carbon monoxide and is converted into *as*-di-*p*-tolylethylene, $C(C_7H_7)_2{:}CH_2$, crystallising in colourless, glistening plates which melt at 61° and is identical with the ditolylethylene obtained as an oil by Hepp (this Journal, 1875, 361). Both products yielded the di-*p*-tolyl ketone melting at 95°, which forms a *phenylhydrazone* crystallising in aggregates of short, yellow prisms and melting at 100°.

αα-Di-o-*xylylpropionic acid*, $CMe(C_6H_3Me_2)\cdot CO_2H$, prepared by the condensation of *o*-xylene and pyruvic acid in concentrated sulphuric acid at −10°, crystallises in colourless, flat prisms arranged in concentric clusters, melts at 149°, and forms a crystalline *barium* salt. as-*Di*-o-*xylylethylene*, $C(C_6H_3Me_2)_2{:}CH_2$, melts at 73—74° and is easily oxidised to 3 : 4 : 3′ : 4′-*tetramethylbenzophenone*, $CO(C_6H_3Me_2)_2$; this melts at 140°, forms an *oxime* crystallising in prisms and melting at 147°, and a *phenylhydrazone* melting at 130°.

2 : 5-*Dimethylatropic acid*, $CH_2{:}C(C_6H_3Me_2)\cdot CO_2H$, prepared from *p*-xylene and pyruvic acid, forms colourless, rhombic plates melting at 130—131°. Carbon monoxide is eliminated by concentrated sulphuric acid from this at 110—120°. *Dimethylatropic acid dibromide*, prepared by brominating the acid in carbon bisulphide solution, crystallises in colourless, short prisms melting at 153°, with elimination of hydrogen bromide.

2 : 5-*Dimethyldihydroatropic acid*, $C_6H_3Me_2\cdot CHMe\cdot CO_2H$, prepared by reducing dimethylatropic acid with sodium amalgam, crystallises in colourless needles and melts at 115—116°.

αα-Di-m-*xylylpropionic acid* crystallises in six-sided, pointed prisms and melts at 168—169°. E. F. A.

Conversion of *allo*Cinnamic Acid into Erlenmeyer's *iso*Cinnamic Acid. Emil Erlenmeyer, jun. (*Ber.*, 1905, 38, 837—838. Compare Abstr., 1896, i, 46; 1904, i, 892).—Both Liebermann (Abstr., 1898, i, 662) and Michael (Abstr., 1902, i, 32) have been unable to convert *allo*cinnamic into *iso*cinnamic acid. The author has repeated Erlenmeyer's experiments, and finds that 0·5 gram of *allo*cinnamic acid, dissolved in alcohol in presence of zinc bromide and kept in the dark during six days, is converted into the characteristic crystals of *iso*cinnamic acid. E. F. A.

Transformation of Racemic Compounds into the Corresponding Optically Active Forms. Willy Marckwald and David M. Paul (*Ber.*, 1905, 38, 810—812).—When an optically active compound with one asymmetric carbon acid is racemised by

heat, equilibrium is established when equal amounts of the two mirror images are present. The case is, however, different in the racemisation by heat of a compound containing two asymmetric carbon atoms, and where interchange of groups takes place only at one of the carbon atoms.

r-Mandelic acid was heated for 10 hours at 150—160° with the amount of anhydrous brucine requisite for the formation of the brucine salt. The product was then dissolved in water, acidified by sulphuric acid, and extracted with ether, when the mandelic acid obtained was found to be feebly dextrorotatory. From this mixture of *d*- and *r*-acids, pure *d*-mandelic acid was isolated by Marckwald and McKenzie's method (Abstr., 1899, ii, 733). A. McK.

Nitrotolylglycollic [Nitrotolyloxyacetic] Acids. Giuseppe Kernot (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1904, [iiia], **10**, 373—381).—The action of concentrated nitric acid of sp. gr. 1·4 on *p*-tolylglycollic acid yields a nitrocresol melting at 77° and *3-nitro-*p*-tolyloxyacetic acid*, $C_9H_9O_5N$ [$O·CH_2·CO_2H : NO_2 : Me = 1 : 3 : 4$], which may also be obtained by the interaction of 3-nitro-*p*-cresol and ethyl chloroacetate, and separates from aqueous alcohol in shining, yellow, flattened needles melting at 140—141°; it is slightly soluble in water, more so in benzene or chloroform, and readily so in alcohol or ether. The *barium* salt [with $3H_2O$] forms aggregates of orange-yellow prisms and the *silver* salt separates from water in aggregates of pale yellow, silky needles almost unalterable by light. The *anilide*,

$$NO_2·C_6H_3Me·O·CH_2·CO·NHPh,$$

crystallises from alcohol in pale yellow, flattened prisms and from benzene in well-defined, rhombic plates melting at 134°. On reduction in alcoholic solution by means of tin and hydrochloric acid, it yields *3-amino-*p*-tolyloxyacetic acid*, $C_9H_{11}O_3N$[$O·CH_2·CO_2H : NH_2 : Me = 1 : 3 : 4$], which crystallises from water in white plates, melts at 200°, changes slowly in the light, and is soluble in alcohol or benzene.

The action of nitric acid on *o*-tolyloxyacetic acid yields a mixture of various nitro-derivatives, together with *6-nitro-*o*-tolyloxyacetic acid* [$O·CH_2·CO_2H : NO_2 : Me = 1 : 6 : 2$], which may also be obtained by the interaction of 6-nitro-*o*-cresol [$Me : OH : NO_2 = 1 : 2 : 6$] and ethyl chloroacetate, and crystallises from aqueous alcohol in shining, yellow needles softening at 128° and melting at 130°; the acid is moderately soluble in benzene or chloroform, and readily so in alcohol or ether. The *barium* salt [with $2H_2O$] crystallises from water in orange-red needles.

*6-Nitro-*m*-tolyloxyacetic acid* [$O·CH_2·CO_2H : NO_2 : Me = 1 : 6 : 3$], prepared either by the action of ethyl chloroacetate on the corresponding nitro-*m*-cresol or by the nitration of *m*-tolyloxyacetic acid, crystallises from aqueous alcohol in prismatic needles melting at 140—141° and dissolves slightly in water, moderately in benzene or chloroform, and readily in ether. T. H. P.

Syntheses with Sodamide. Ludwig Claisen [and, in part, R. Feyerabend, R. Schulze, and R. Gärtner] (*Ber.*, 1905, **38**, 693—709).—Sodamide may be used profitably as a substitute for

sodium ethoxide in the condensation of ketones with esters; in many cases, the action occurs more readily and more rapidly than that of the ethoxide, and a better yield is obtained. This was found to hold in condensing ethyl acetate and ethyl benzoate with acetone and with acetophenone respectively, and in the preparation of hydroxymethylene ketones. On the other hand, the use of sodamide does not give good results in the condensation of ketones with esters of nitrous acid, but the mono-alkylation of ketones is more readily effected by the action of sodamide on a cold ethereal solution of the ketone and alkyl iodide than by Nef's method; using this process, ethylacetophenone and benzylacetophenone can be readily obtained.

The action of sodamide on an ethereal solution of ethyl chloroacetate and acetophenone probably takes place in three stages, as follows:

$$\text{I. } COPhMe + NaNH_2 \longrightarrow ONa{\cdot}CPhMe{\cdot}NH_2.$$

$$\text{II. } ONa{\cdot}CPhMe{\cdot}NH_2 + CH_2Cl{\cdot}CO_2Et \longrightarrow ONa{\cdot}CPhMe{\cdot}CHCl{\cdot}CO_2Et.$$

$$\text{III. } ONa{\cdot}CPhMe{\cdot}CHCl{\cdot}CO_2Et \longrightarrow NaCl + \begin{matrix} CPhMe \\ | \\ O \end{matrix} \!\!>\! CH{\cdot}CO_2Et.$$

Ethyl β-phenyl-β-methylglycidate, $\begin{matrix} CPhMe \\ | \\ O \end{matrix}\!\!>\! CH{\cdot}CO_2Et$, is a colourless, somewhat viscid liquid which boils at 147—149° under 12 mm. and at 272—275° under the ordinary pressure; it has a sp. gr. 1·096 at 15°. The analogous *methyl* ester, $C_9H_9O{\cdot}CO_2Me$, prepared from methyl chloroacetate, has a sp. gr. 1·129 at 15°, and boils at 141—143° under 11 mm. and at 269—272° under the ordinary pressure. The *sodium* salt, $\begin{matrix} CPhMe \\ | \\ O \end{matrix}\!\!>\! CH{\cdot}CO_2Na$, obtained by mixing the ethyl ester with sodium ethoxide dissolved in absolute alcohol and then adding water (1 mol.), forms white leaflets and melts and decomposes at 256°; the crystalline *barium* salt is rapidly decomposed by warm water and the *silver* salt is amorphous. The *amide*, $C_9H_9O{\cdot}CO{\cdot}NH_2$, crystallises from hot water in lustrous needles and melts at 168°; an isomeric *amide* is formed with it which crystallises from methyl alcohol in prisms or leaflets and melts at 151°.

When β-phenyl-β-methylglycidic acid is liberated from its sodium salt by adding acids, it at once decomposes, giving hydratropaldehyde (α-phenylpropaldehyde), CHPhMe·CHO (von Müller and Rohde, Abstr., 1891, 898), which boils at 203—205° and has a sp. gr. 1·012 at 15°; the *semicarbazone*, $C_{10}H_{13}ON_3$, crystallises from dilute alcohol in nacreous leaflets and melts at 153°; the *imino*-derivative, CPhMe·CH:NH, obtained by the direct action of aqueous ammonia on the aldehyde, separates from alcohol as a micro-crystalline powder and melts when rapidly heated at 114°. Ethyl β-phenyl-β-methylglycidate combines with hydrogen bromide to form *ethyl β-bromo-α-hydroxy-β-phenylbutyrate*, $CPhMeBr{\cdot}CH(OH){\cdot}CO_2Et$, which crystallises in needles from light petroleum containing benzene and melts at 82—83°.

Ethyl β-phenyl-β-ethylglycidate, $\begin{matrix} CPhEt \\ | \\ O \end{matrix}\!\!>\! CH{\cdot}CO_2Et$, prepared from phenyl ethyl ketone and ethyl chloroacetate in presence of sodamide,

boils at 148—150° under 12 mm. pressure and has a sp. gr. 1·072 at 15°.

Ethyl ββ-dimethylglycidate, $C_2H_{12}O_3$, prepared from acetone, boils at 180—182° and has a sp. gr. 1·016 at 15°; *sodium ββ-dimethylglycidate* crystallises in leaflets.

Ethyl β-methyl-β-ethylglycidate, $C_8H_{14}O_3$, obtained from methyl ethyl ketone, boils at 84—86° under 10 mm. and at 197—199° under the ordinary pressure; it has a sp. gr. 1·001 at 15°.

Ethyl β-methyl-β-propylglycidate boils at 91—92° under 11—12 mm. and at 211—212° under the ordinary pressure.

Ethyl ββ-diethylglycidate boils at nearly the same temperature as ethyl β-methyl-β-propylglycidate and has a sp. gr. 0·993 at 15°.

When benzaldehyde is condensed with ethyl chloroacetate under the influence of sodamide, ethyl β-phenylglycidate is the principal product, but some ethyl α-chlorocinnamate is also formed (compare E. Erlenmeyer, jun., Abstr., 1893, i, 36). W. A. D.

Nitro-derivatives of β-Resorcylic Acid [2:4-Dihydroxybenzoic Acid]. FRANZ VON HEMMELMAYR (*Monatsh.*, 1905, **26**, 185—198. Compare Abstr., 1904, i, 319).—When heated with water at 160° in a sealed tube, nitro-β-resorcylic acid yields 4-nitroresorcinol, and must therefore be 5-nitro-2:4-dihydroxybenzoic acid.

The action of fuming nitric acid on nitro-β-resorcylic acid leads to the formation of 3:5-*dinitro*-2:4-*dihydroxybenzoic acid*, $C_7H_4O_8N_2$, which crystallises in clusters of flat, yellow needles, becomes colourless on exposure to the air, commences to sinter and to sublime at 180°, and melts at 205°. The *diammonium*, *potassium*, *dipotassium*, *barium*, $C_7H_2O_8N_2Ba,2H_2O$, and the *disilver* salts are described. When boiled with water in a reflux apparatus, the dinitro-acid loses carbon dioxide and yields 2:4-dinitroresorcinol, which melts at 147—148° (m. p. 145°, Lippmann and Fleissner, Abstr., 1886, **235**, 791), and, when warmed with dilute nitric acid, yields styphnic acid. The barium derivative, $C_6H_2O_2(NO_2)_2Ba,H_2O$, obtained by boiling 2:4-dinitroresorcinol with barium carbonate in aqueous solution, forms a reddish-yellow, crystalline, flocculent precipitate and loses H_2O at 130°; the barium derivative, $C_6H_2O_6N_2Ba,4H_2O$, formed by the action of barium chloride on the ammonium derivative of dinitroresorcinol, crystallises in microscopic, flat, yellow needles, loses $3H_2O$ at 130°, and H_2O at 180° (compare Bendikt, *Monatsh.*, 1881, **2**, 324; Lippmann and Fleissner, *loc. cit.*).

In concentrated solution and with rapid cooling, styphnic acid forms a brownish-red, anhydrous, crystalline silver salt (compare Abstr., 1904, i, 814). G. Y.

A New Reaction of Aldehydes, and the Isomerism of their Oximes. A. CONDUCHÉ (*Compt. rend.*, 1905, **140**, 434—436).—Benzaldehyde condenses with *iso*hydroxycarbamide (a molecular mixture of hydroxylamine hydrochloride and potassium cyanate, compare Francesconi and Parrozzani, Abstr., 1902, i, 139) to form a well-defined crystalline *compound*, $O<\begin{matrix}CHPh\\ | \\ N\cdot CO\cdot NH_2\end{matrix}$, melting at 125°, and similar compounds, produced from anisaldehyde, *m*-nitrobenzaldehyde,

furfuraldehyde, and heptaldehyde melting at 132°, 172°, 144°, and 85° respectively. The compound from salicylaldehyde decomposes at 100°. The compound from benzaldehyde is reduced by aluminium amalgam forming benzylcarbamide, and is decomposed by hydrochloric acid in aqueous solution, forming benzaldehyde and ammonium chloride, or in alcoholic solution yielding benzamide hydrochloride, ammonium chloride, and carbon dioxide. By the action of dilute aqueous or alcoholic potassium hydroxide, the benzaldehyde compound is converted into β-benzaldoxime and potassium cyanate, and in view of the fact that potassium cyanate condenses with β-benzaldoxime hydrochloride to give the benzaldehyde compound described above, whilst it does not react with the α-isomeride, the author maintains that the isomerism between the two benzaldoximes is structural and not spatial, and represents the formation of β-benzaldoxime from the benzaldehyde compound by the following equation :

$$O<\begin{matrix}CHPh\\ |\\ N\cdot CO\cdot NH_2\end{matrix} + KOH = O<\begin{matrix}CHPh\\ |\\ NH\end{matrix} + CO\cdot NK + H_2O.$$

M. A. W.

Additive Compounds of Hydrogen Bromide and Aromatic Carbonyl Compounds. THEODOR ZINCKE and G. MÜHLHAUSEN (*Ber.*, 1905, **38**, 753—760. Compare Abstr., 1903, i, 265; Vorländer, Abstr., 1903, i, 495; 1904, i, 65, 535, 900; Straus, Abstr., 1904, i, 899; Rosenheim and Levy, Abstr., 1904, i, 1024).—Diphenylbutadiene (diphenyldiethylene) and benzophenone do not form additive compounds with hydrogen bromide. When acted on by anhydrous hydrogen bromide, benzylideneacetone and dibenzylideneacetone are completely converted into resins, but in the presence of moisture the orange-red hydrobromides are formed.

p-Hydroxybenzaldehyde absorbs nearly 2 mols. of hydrogen bromide forming a white product. The action of hydrogen bromide on p-hydroxyacetophenone, in the solid state or dissolved in a mixture of chloroform and ether, leads to the formation of the colourless crystalline *hydrobromide*, $C_8H_8O_2,HBr$. p-Hydroxybenzophenone, with hydrogen bromide in ethereal solution, forms the yellow, crystalline *hydrobromide*, $C_{13}H_{10}O_2,HBr$, which yields p-hydroxybenzophenone when treated with water. In the solid state or in solution, p-hydroxybenzylideneacetone and p-dihydroxydibenzylideneacetone form coloured additive compounds with hydrogen bromide; these, when placed over potassium hydroxide, lose part of the hydrogen bromide, yielding the hydrobromides, $(C_{10}H_{10}O_2)_2,HBr$ and $C_{17}H_{14}O_3,HBr$. G. Y.

Benzophenonesulphone. FRITZ ULLMANN and ALFRED LEHNER (*Ber.*, 1905, **38**, 729—742. Compare Abstr., 1904, i, 417).—Tröger and Voigtländer-Tetzner (Abstr., 1897, i, 223), for the preparation of o-toluenesulphonic bromide, and Canter (Abstr., 1901, i, 208), for the preparation of phenyl-o-tolylsulphone, made use of commercial o-toluenesulphonic chloride containing 30 per cent. of the para-compound, and therefore obtained mixtures of ortho- and para-products.

o-Toluenesulphonic chloride, prepared by the action of chlorine on potassium o-toluenesulphinate in aqueous solution, distils at 126°

under 10 mm. pressure and has a sp. gr. 1·3413 at 17°. *o*-Toluenesulphonic bromide, prepared by the action of bromine on *o*-toluenesulphinic acid in aqueous solution, melts at 13°, boils at 137·5—138° under 10 mm. pressure, and when shaken with aniline and aqueous sodium hydroxide forms *o-toluenesulphanilide*, $C_{13}H_{13}O_2NS$, which separates from benzene in small, colourless crystals and melts at 134°.

Phenyl-*o*-tolylsulphone, prepared by the action of aluminium chloride on *o*-toluenesulphonic chloride in benzene solution, forms small, glistening crystals, melts at 80°, and is oxidised by potassium permanganate in aqueous solution to diphenylsulphone-*o*-carboxylic acid, which melts at 144° (m. p. 152°; Graebe and Schultess, Abstr., 1891, 1058), and when heated in concentrated sulphuric acid at 180—190° yields benzophenonesulphone (Beckmann, *Ber.*, 1873, **6**, 1112).

Phenyl-p-*acetylamino*-o-*tolylsulphone*, $NHAc\cdot C_6H_3Me\cdot SO_2Ph$, obtained by treating the amine (Norris, Abstr., 1901, i, 134) with acetic anhydride and glacial acetic acid, crystallises in colourless needles, melts at 183°, and when oxidised with potassium permanganate in aqueous solution yields 5-*acetylaminodiphenylsulphone*-2-*carboxylic acid*, $SO_2Ph\cdot C_6H_3(NHAc)\cdot CO_2H$, which forms yellow crystals and melts and decomposes at 212°.

4′-*Chlorodiphenylsulphone-2-carboxylic acid*, $C_6H_4Cl\cdot SO_2\cdot C_6H_4\cdot CO_2H$, is obtained as the *potassium* salt by heating potassium *o*-chlorobenzoate and *p*-chlorobenzenesulphinate with a trace of copper in aqueous solution at 135°; it crystallises in colourless leaflets. The acid crystallises in glistening, silky needles, melts at 151°, is easily soluble in alcohol, ether, or glacial acetic acid, and when heated with concentrated sulphuric acid at 195°, or when heated to 220—230° with phosphorus pentachloride, yields 3-*chlorobenzophenonesulphone*,

$$C_6H_4<\begin{array}{l}SO_2\cdot C\cdot CH\colon CH\\ CO-C\cdot CH\colon CCl\end{array}.$$

This crystallises in yellow needles, melts at 222°, and gives a blue coloration when warmed with zinc dust and sodium hydroxide in alcoholic solution.

2′-*Methyldiphenylsulphone-2-carboxylic acid*, $C_7H_7\cdot SO_2\cdot C_6H_4\cdot CO_2H$, obtained by the condensation of potassium *o*-chlorobenzoate and *o*-toluenesulphinate in presence of copper, crystallises in large, colourless prisms, melts at 189°, is easily soluble in alcohol, glacial acetic acid, or boiling benzene, and when heated with concentrated sulphuric acid at 190° yields 5-methylbenzophenonesulphone, $C_{14}H_{10}O_3S$, which crystallises in leaflets, melts at 172°, and gives the characteristic blue coloration with zinc dust and sodium hydroxide in alcoholic solution.

4′-*Methyldiphenylsulphone-2-carboxylic acid*, obtained from *o*-chlorobenzoic and *p*-toluenesulphinic acids, melts at 155° and is soluble in alcohol, glacial acetic acid, boiling ether, or benzene. The *methyl* ester, $C_{15}H_{14}O_4S$, crystallises in colourless prisms and melts at 89°. 3-*Methylbenzophenonesulphone*, obtained by heating 4′-methyldiphenylsulphone-2-carboxylic acid in concentrated sulphuric acid, crystallises in yellow needles and melts at 199°. G. Y.

Formation of Salts of Benzoin. JAKOB MEISENHEIMER (*Ber.*, 1905, **38**, 874—878).—The sodium derivative of benzoin has not the formula $C_{42}H_{32}O_5Na_2$ attributed to it by Garner (this vol., i, 143), but when obtained pure, by carrying out the action between sodium and benzoin in an atmosphere of hydrogen, has the composition $C_{28}H_{23}O_4Na$. It is thus formed by the elimination of 1H from two mols. of benzoin, and is decomposed by water or acids quantitatively into the latter; in solution in presence of a slight excess of alkali, it is rapidly oxidised to benzoic acid and benzil, traces of benzilic acid being also formed.

Acetyl chloride converts it into benzoin and acetylbenzoin in molecular ratio, but alkyl iodides do not interact with it at all readily.

p-*Nitrobenzoylbenzoin*, $C_{21}H_{15}O_5N$, prepared from benzoin and *p*-nitrobenzoyl chloride, crystallises from benzene in yellow prisms, melts at 123°, and is converted by boiling sodium methoxide solution into benzil, several other substances having high melting points being also formed at the expense of the *p*-nitrobenzoic acid. W. A. D.

Condensation of Dibenzyl Ketone with Aldehydes under the Influence of Hydrochloric Acid. RICHARD HERTZKA (*Monatsh.*, 1905, **26**, 227—242. Compare Goldschmiedt and Knöpper, Abstr., 1898, i, 31; 1899, i, 140).—*Chloro*-p-*methoxybenzyldibenzyl ketone* (δ-*chloro-αγ-diphenyl*-δ-p-*methoxyphenyl-β-butanone*),

$$OMe\cdot C_6H_4\cdot CHCl\cdot CHPh\cdot CO\cdot CH_2Ph,$$

formed by the action of hydrogen chloride on a mixture of dibenzyl ketone and anisaldehyde cooled by ice, crystallises in rhombic plates, melts at 120—121°, and dissolves in concentrated sulphuric acid to a red solution, which, when diluted with water, yields a white flocculent precipitate.

αγ-Diphenyl-δ-p-*methoxyphenyl-Δ^γ-butylene-β-one*,

$$OMe\cdot C_6H_4\cdot CH:CPh\cdot CO\cdot CH_2Ph,$$

formed when *p*-methoxychlorobenzyldibenzyl ketone is heated at 140—160° under 12 mm. pressure or is treated with cold alcoholic potassium hydroxide, crystallises in white needles and melts at 98°.

δ-*Methoxy-αγ-diphenyl*-δ-p-*methoxyphenyl-β-butanone*,

$$OMe\cdot C_6H_4\cdot CH(OMe)\cdot CHPh\cdot CO\cdot CH_2Ph,$$

is formed when *p*-methoxychlorobenzyldibenzyl ketone is boiled with methyl alcohol; it crystallises in colourless, rhombic prisms, melts at 118—120°, and dissolves in concentrated sulphuric acid to a red solution. δ-*Ethoxy-αγ-diphenyl*-δ-p-*methoxyphenyl-β-butanone*, obtained in the same manner by the action of ethyl alcohol, crystallises in rhombic plates and melts at 92°.

δ-*Chloro-αγ-diphenyl*-δ-m-p-*methylenedioxyphenyl-β-butanone*,

$$CH_2:O_2:C_6H_3\cdot CHCl\cdot CHPh\cdot CO\cdot CH_2Ph,$$

formed by the action of hydrogen chloride on a mixture of dibenzyl ketone and piperonal, is obtained as a white, crystalline mass, melts and decomposes at 106°, and dissolves in concentrated sulphuric acid to a brown solution, becoming violet on dilution. When heated at 130—150° under 12 mm. pressure, it yields *αγ-diphenyl*-δ-m-p-*methylenedioxyphenyl-Δ^γ-butene-β-one*, $CH_2:O_2:C_6H_3\cdot CH:CPh\cdot CO\cdot CH_2Ph$, which crystallises in yellow needles, melts at 120°, and dissolves in con-

centrated sulphuric acid to a red solution. *δ-Methoxy-αγ-diphenyl-δ-*m-p*-methylenedioxyphenyl-β-butanone*,

$$CH_2{:}O_2{:}C_6H_3{\cdot}CH(OMe){\cdot}CHPh{\cdot}CO{\cdot}CH_2Ph,$$

obtained by boiling the chloro-compound in methyl alcohol, crystallises in needles and melts at 97°; the corresponding *ethoxy*-compound forms nodular crystals and melts at 87°.

α-Chlorocinnamenyldibenzyl ketone,

$$CHPh{:}CH{\cdot}CHCl{\cdot}CHPh{\cdot}CO{\cdot}CH_2Ph,$$

formed by the condensation of dibenzyl ketone with cinnamaldehyde in presence of hydrogen chloride, melts at 107°. n-*Chlorobutyldibenzyl ketone*, obtained by the condensation of dibenzyl ketone with *n*-butaldehyde, forms white crystals and melts at 76°. G. Y.

Condensation of Phenylacetone with Phenanthraquinone. Hugo Lang (*Monatsh.*, 1905, **26**, 199—215. Compare Japp and Klingemann, Trans., 1891, **59**, 11; Goldschmiedt and Knöpper, Abstr., 1898, i, 31; 1899, i, 140).—When warmed with piperidine or potassium hydroxide in alcoholic solution, phenylacetone and phenanthraquinone condense to phenanthroxylenephenylacetone; if the condensation takes place in the presence of a small quantity of aqueous potassium hydroxide only, in addition to phenanthroxylenephenylacetone, traces of an *isomeride*, which crystallises in yellow needles and melts at 196°, are formed.

Phenanthroxylenephenylacetone, $\begin{array}{l}C_6H_4{\cdot}C{=\!=\!=}CPh\\ \,|\qquad\ \ |\\ C_6H_4{\cdot}C(OH){\cdot}CH_2\end{array}\!\!>\!CO$, crystallises in long, pale green needles, melts with slight decomposition at 188°, is easily soluble in chloroform, hot alcohol, ether, or benzene, but is insoluble in water, dilute acids, or aqueous alkali hydroxides, dissolves in concentrated sulphuric acid to an intensely bluish-green solution, and condenses with benzaldehyde in alcoholic potassium hydroxide solution to a *benzylidene* derivative, $C_{30}H_{20}O_2$, which crystallises in yellow needles and melts with slight decomposition at 234°.

The *phenylhydrazone*, $C_{29}H_{22}ON_2$, crystallises in long, reddish-brown needles and melts and decomposes at 181—184°; the *dibromide*, $C_{23}H_{16}O_2Br_2$, crystallises in rhombic plates, commences to decompose at 150°, and is completely melted at 175°. When boiled with zinc and hydrochloric acid in alcoholic solution, phenanthroxylenephenylacetone is reduced to 1-*phenyl*-2 : 3-o-*diphenylene*cyclo*pentanone*, $\begin{array}{l}C_6H_4{\cdot}CH{\cdot}CHPh\\ \,|\qquad\ |\\ C_6H_4{\cdot}CH{-}CH_2\end{array}\!\!>\!CO$, which crystallises in hexagonal plates, commences to decompose at 190°, melts at 233—236°, is easily soluble in hot benzene or chloroform, but only slightly so in water, alcohol, or ether, and dissolves in concentrated sulphuric acid to a yellowish-green solution; the *phenylhydrazone*, $C_{29}H_{24}N_2$, crystallises in brown needles and melts and decomposes at 220—222°.

When boiled with dilute sulphuric acid in a reflux apparatus, phenanthroxylenephenylacetone is converted into iso*phenanthroxylenephenylacetone*, $\begin{array}{l}C_6H_4{\cdot}CH{=\!=\!=}CH\\ \,|\qquad\ \ |\\ C_6H_4{\cdot}C(OH){\cdot}CHPh\end{array}\!\!>\!CO$, which crystallises in slender, white prisms, melts with slight decomposition at 202°, is easily soluble

in benzene, carbon disulphide, or pyridine, and dissolves in concentrated sulphuric acid to a green solution; it decolorises alkaline potassium permanganate solution, and is reduced by zinc dust and hydrochloric acid in benzene solution to 1-phenyl-2 : 3-*o*-diphenyl*cyclo*pentanone. The *phenylhydrazone*, $C_{29}H_{22}ON_2$, crystallises in clusters of long, slender, red needles, commences to decompose at 150°, and melts at 191°; the *dibromide*, $C_{23}H_{16}O_2Br_2$, crystallises in yellow leaflets and melts at 192°. G. Y.

Cinnamylidenecamphor and its Reduction Products. JULIUS W. BRÜHL (*Ber.*, 1905, **38**, 760—761).—A criticism of Rupe and Frisell's paper (this vol., i, 220). G. Y.

Gutta-percha-like Substance from the Resin of the Karite Tree. FRITZ FRANK and EDUARD MARCKWALD (*Chem. Centr.*, 1905, i, 186; from *Gummi Zeit.*, 1904, **19**, 167).—The resin of the Karite or Shea butter tree (*Bassia* or *Butyrospermum Parkii*) has the percentage composition gutta-percha 25·2, resin 57·13, plant constituents 5·76, mineral components 6·87, and water 5·04. The gutta substance, after purification, contains 8·31 per cent. of oxygen, and behaves like gutta-percha towards solvents. The nitrogen peroxide compound gave figures agreeing with those of Harries' nitrosite "c," $(C_{10}H_{16}O_7N_3)_2$.

The resin soluble in acetone is separated by extraction with acetone or alcohol into a resin of high melting point and a gummy resin. The resin has an odour of cinnamon, especially on boiling the less fusible fraction with potassium hydroxide, and probably yields cinnamic acid and lupeol. G. D. L.

[Theory of Dyeing.] P. D. ZACHARIAS (*Ber.*, 1905, **38**, 816).—Polemical. A reply to Biltz (this vol., i, 224). A. McK.

Red Colouring Matter of Tomatoes. CARLO MONTANARI (*Chem. Centr.*, 1905, i, 544; from *Staz. sperim. agrar. ital.*, 1904, **37**, 909—919. Compare Arnaud, Abstr., 1886, 712).—After removal of the seeds and skin and treatment with alcohol, the red colouring matter was extracted with carbon disulphide. After purification according to the method described by Arnaud, it crystallises from benzene in the form of deep red lamellæ and needles melting at 170°. On addition of iodine to the benzene solution, an amorphous, green precipitate of the composition $C_{52}H_{74}I_2$ separates. From this, it is concluded that the red colouring substance has the formula $C_{52}H_{74}$. Cryoscopic determinations of the molecular weight in benzene solution gave 635 and 650 (calculated for $C_{52}H_{74}$, 698). The substance is therefore not identical with carrotene, $C_{26}H_{38}$, the colouring matter of carrots, but is to be regarded as a dicarrotene. H. M. D.

Composition of Certain Invertebrate Pigments. ARTHUR B. GRIFFITHS (*Chem. News*, 1905, **91**, 90—91. Compare Abstr., 1900, ii, 677; 1901, i, 94).—The red pigments of *Actinia mesembryanthemum* and of Ophiuroidea were isolated by treating the ethereal solutions with *N*/100 sodium hydroxide and evaporating in a vacuum.

The actinia pigment has the composition $C_8H_9O_3N$ and in ethereal solution has $[\alpha]_D - 70{\cdot}19°$ at 18°. The Ophiuroidea pigment has the composition $C_{25}H_{24}O_3N_2$; it is soluble in ether, alcohol, chloroform, or benzene and when boiled with oxidising agents yields leucine and formic acid. The solution in ether has $[\alpha]_D - 97{\cdot}84°$ at 17°. The absorption spectra of both pigments are described and other red pigments from the animal kingdom are mentioned. D. A. L.

Synthesis of Chroman. JULIUS VON BRAUN and A. STEINDORFF (*Ber.*, 1905, **38**, 850—855).—*o*-γ-Chloropropylbenzanilide (Abstr., 1904, i, 918), when treated with hydrochloric acid for 3—4 hours at 125—130°, gives o-γ-*chloropropylaniline hydrochloride*,

$$CH_2Cl{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}NH_2,HCl,$$

which crystallises in thick needles, melts and decomposes at 161°, and gives a corresponding *platinichloride* and *aurichloride*; on adding alkali to the hydrochloride, the base $CH_2Cl{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}NH_2$ is first separated but this rapidly undergoes transformation into tetrahydroquinoline hydrochloride. o-γ-*Chloropropylphenol*, prepared from *o*-γ-chloropropylaniline sulphate by means of the diazo-reaction, boils at 150—151° under 13 mm. pressure, undergoing partial decomposition; with phenylcarbimide, it gives the *phenylcarbamate*, $C_{16}H_{16}O_2NCl$, which crystallises from light petroleum in globular aggregates of needles and melts at 74—76°. *Chroman*, $C_6H_4{<}\begin{matrix}CH_2{\cdot}CH_2\\ O \text{——} CH_2\end{matrix}$, prepared by warming an alkaline solution of *o*-γ-chloropropylphenol, boils at 214—215° under 749 mm. pressure and has an odour like peppermint. W. A. D.

Coumarin Derivatives from Ethyl *o*-Carboxy-phthalyl- and -benzyl-acetoacetates. CARL BÜLOW [with ERWIN SIEBERT] (*Ber.*, 1905, **38**, 474—486. Compare Abstr., 1904, i, 609, 610).—7-*Hydroxy*-4-*methyl*-1 : 2-*benzopyrone*-3-o-*phthalaldehydic acid* [7-*hydroxy*-4-*methyl*-1 : 2-*benzopyrone*-3-*benzoyl*-o-*carboxylic acid*],

$$OH{\cdot}C_6H_3{<}\begin{matrix}O\text{——}CO\\ CMe{:}C{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H\end{matrix},$$

or the isomeric lactone obtained by the condensation of ethyl phthalylacetoacetate with resorcinol by means of dry hydrogen chloride in glacial acetic acid solution, crystallises from alcohol in colourless needles, melts at 180°, and is insoluble in water, ether, benzene, or light petroleum, and also in dilute sodium carbonate, yielding a yellow solution; this colour disappears to a large extent on the addition of a few drops of sodium hydroxide solution and subsequent heating at 50°. When fused for a few minutes with potassium hydroxide at 180—190°, the benzopyrone derivative yields resorcinol, resacetophenone, phthalic acid, and acetic acid. The formation of resacetophenone is made use of in supporting the constitutional formula already given.

The *acetate*, $OAc{\cdot}C_6H_3{<}\begin{matrix}O\text{——}CO\\ CMe{:}C{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H\end{matrix}$, melts at 152° and is insoluble in water, ether, or light petroleum and also in alkalis or alkali carbonate solutions.

A good yield of 5 : 7-*dihydroxy*-4-*methyl*-1 : 2-*benzopyrone*-3-o-*phthalaldehydic acid* [5 : 7-*dihydroxy*-4-*methyl*-1 : 2-*benzopyrone*-3-*benzoyl*-o-

carboxylic acid], $C_{18}H_{12}O_7$, is obtained from ethyl phthalylacetoacetate and phloroglucinol; it resembles the 7-hydroxy-derivative, and its solutions in dilute sodium carbonate have an orange-yellow colour. When dissolved in very dilute sodium hydroxide, the colour of the solution is first orange-yellow, but quickly changes to pale yellow. The isomeric 7:8-*dihydroxy*-derivative, obtained from pyrogallol, crystallises from alcohol or acetic acid and melts at 237°. Its solution in dilute sodium carbonate has a pure victoria-blue or light blue colour, which is almost completely removed by warming with sodium hydroxide, probably owing to its conversion into β-methyldaphnetin-α-benzoyl-*o*-carboxylic acid.

Ethyl *o*-carboxybenzylacetoacetate also condenses with resorcinol yielding *7-hydroxy-4-methyl-1:2-benzopyrone-3-o-benzylcarboxylic acid*, $OH\cdot C_6H_3 <\begin{matrix} O——CO \\ CMe:C\cdot CH_2\cdot C_6H_4\cdot CO_2H \end{matrix}$, which crystallises from alcohol in small, colourless needles melting at 283°, or from glacial acetic acid in hexagonal prisms. Its solutions in dilute alkalis have a blue fluorescence resembling that of Pechmann and Duisberg's β-methylumbelliferone. It is not precipitated from its alkaline solutions by means of carbon dioxide, and when boiled with 10 per cent. potassium hydroxide it yields resorcinol and benzylacetone-*o*-carboxylic acid (Abstr., 1887, 144); when fused with potassium hydroxide at 285—295° it yields resorcinol, resacetophenone, *o*-toluic acid, and acetic acid.

The *acetyl* derivative, $OAc\cdot C_6H_3 <\begin{matrix} O——CO \\ CMe:C\cdot CH_2\cdot C_6H_4\cdot CO_2H \end{matrix}$, melts at 246—247°. The 5:7-*dihydroxy*- and 7:8-*dihydroxy*-compounds have both been prepared; the latter melts at 259—260°. J. J. S.

The Oxidising Action of Impure Ether. A. I. Rossolimo (*Ber.*, 1905, **38**, 774—775. Compare Decker, Abstr., 1903, i, 516; Berthelot, Abstr., 1881, 709).—When aqueous solutions of caffeine alkyl iodides are extracted with crude ether, a crystalline precipitate of a periodide is obtained. The formation is probably due to the oxidising action of a minute quantity of ethyl peroxide on the iodide, and it has been found that even a small amount of impure ether is capable of decomposing the whole of the caffeine alkyl iodide. The ether was a specimen of pure ether left in a wash-bottle for three months in contact with atmospheric oxygen. J. J. S.

Crystalline Alkaloid of Calycanthus Glaucus. Harry M. Gordin (*J. Amer. Chem. Soc.*, 1905, **27**, 144—155).—Calycanthine, the alkaloid obtained from the seeds, or rather achenes, of *Calycanthus glaucus*, was first described by Eccles (*Proc. Amer. Pharm. Assoc.*, 1888, **84**, 382) and afterwards studied by Wiley (Abstr., 1890, 403).

After the oil has been extracted from the seeds, the residue contains about 2 per cent. of calycanthine. The alkaloid, $C_{11}H_{14}N_2,\frac{1}{2}H_2O$, crystallises in orthorhombic bipyramids and melts at 216—218°; if heated for 3 or 4 hours at 120°, it becomes anhydrous and then melts at 243—244°. Calycanthine has a bitter taste, a slightly alkaline reaction towards litmus, and is very slightly soluble in water, but

readily so in ether or chloroform. The *hydrochloride, hydrobromide, hydriodide, sulphate, platinichloride, aurichloride, acetate,* and *picrate* are described. A list is given of various colour reactions which can be employed for the identification of the alkaloid.

Physiological experiments have shown that calycanthine produces symptoms similar to those brought about by strychnine. The alkaloid appears to act as a stimulant to the spinal cord and a depressant to the heart, and there is no doubt that it is the principal poisonous constituent of the seeds. E. G.

Constitution of *α-iso-ψ*-Cinchonicine and of *β-iso*Cinchonicine. KARL KAAS (*Monatsh*, 1905, **26**, 119—125. Compare this vol., i, 151; Skraup and Zwerger, Abstr., 1902, i, 305, 726).—When treated with methyl iodide in ethereal solution, *α-iso-ψ*-cinchonicine forms the *hydriodide* of the methyl base, $C_{19}H_{21}ON_2Me,HI$, which decomposes at 248°, and when treated successively with ammonia and hydrochloric acid is converted into the *hydrochloride.* This is also obtained by heating *α-iso*cinchonine methiodide with aqueous potassium hydroxide and treating the product with hydrochloric acid; it crystallises in rosettes of slender, white needles. *α-iso-ψ*-Cinchonicine must be a keto-base, as its relation to *α-iso*cinchonine is the same as that of cinchonicine to cinchonine.

*β-iso*Cinchonicine dissolved in a mixture of chloroform and alcohol was treated with bromine, and, after one day, with ammonia; on extraction with ether and saturation of the ethereal solution with hydrogen chloride, the *hydrochloride* of the additive product with hydrogen bromide, $C_{19}H_{22}ON_2,HBr,2HCl$, is obtained as a yellow precipitate. The treatment of *α-iso-ψ*-cinchonicine with chlorine in concentrated hydrochloric acid solution leads in a similar manner to the formation of the *hydrochloride* of the additive compound with hydrogen chloride, $C_{19}H_{22}ON_2,HCl,2HCl$, which is obtained as a yellow hygroscopic precipitate. *α-iso-ψ*-Cinchonicine and *β-iso*cinchonicine therefore probably contain a vinyl group. G. Y.

Isomeric Coninium Iodides. II. MAX SCHOLTZ (*Ber.*, 1905, **38**, 595—600. Compare Abstr., 1904, i, 1044).—The isomeric coninium iodides described in the first communication were prepared from coniine, which was purified by means of the hydrochloride and had $[\alpha]_D$ 14·8°. The coniine, used for the preparation of the salts now described, was purified by crystallisation of its hydrogen tartrate and had $[\alpha]_D + 15·5°$, a value in agreement with that of Ladenburg for the naturally occurring product. The action of benzyl iodide on 1-ethylconiine and on 1-*iso*amylconiine respectively was repeated, the latter specimen of coniine being used; the results previously obtained were confirmed.

α-Benzylethylconinium iodide, melting at 179°, is transformed at this temperature into the *β*-isomeride melting at 208°, the transformation apparently being complete. The reverse change does not take place. The physiological action of the two isomerides is also different, as also is that of the isomeric benzylpropyl-, benzylbutyl-, and benzyl*iso*amylconinium iodides respectively.

1-Ethylconiine combines with allyl iodide to form a mixture of two isomeric coninium iodides, which are separated by fractional precipitation of the alcoholic solution of the mixture with ether.

α-Ethylallylconinium iodide, $C_8H_{16}\colon NEtI\cdot C_3H_5$, is readily soluble in cold water, crystallises in microscopic prisms, and melts at 175°. *β-Ethylallylconinium iodide* is more sparingly soluble in water than the α-form, crystallises in needles, and melts at 191°.

Diallylconinium iodide, $C_{14}H_{26}NI$, prepared by the action of allyl iodide on coniine, separates from a mixture of alcohol and ether in leaflets and melts at 183°.

Dipropylconinium iodide, obtained as a by-product from the preparation of 1-propylconiine by interaction of coniine, propyl iodide, and potassium hydroxide, separates from a mixture of alcohol and ether in leaflets and melts at 219°.

The mixture of isomerides formed by the action of benzyl iodide on 1-propylconiine may be separated by water or by acetone, in either of which solvents the α-form is the more soluble. *α-Benzylpropylconinium iodide*, $C_{18}H_{30}NI$, separates from a mixture of alcohol and ether in needles and melts at 159°. *β-Benzylpropylconinium iodide* separates from water in microscopic prisms and melts at 196°.

1-*Butylconiine*, prepared from coniine, *n*-butyl iodide, and potassium hydroxide, boils at 223—224° (corr.) and has a sp. gr. 0·8393 at 20°/4° and $[\alpha]_D$ 72·6°. The separation of the isomerides formed by the action of benzyl iodide on 1-butylconiine is effected with some difficulty by means of acetone. *α-Benzylbutylconinium iodide*, $C_{19}H_{32}NI$, separates from water in needles and melts at 167—169°. *β-Benzylbutylconinium iodide* melts at 188°.

Crystallographic data respecting the isomeric benzyl*iso*amylconinium iodides and the benzylethylconinium iodides are quoted.

A. McK.

Lysine. Max Siegfried (*Zeit. physiol. Chem.*, 1905, **43**, 363—364. Compare Abstr., 1891, 591).—*d*-Lysine platinichloride has the composition $C_6H_{14}O_2N_2,H_2PtCl_6,EtOH$, and *dl*-lysine platinichloride

$$C_6H_{14}O_2N_2,H_2PtCl_6.$$

The preparation and analysis of the platinichlorides is recommended as a method for isolating lysine and also for distinguishing between *d*- and *dl*-lysine.

J. J. S.

[Zirconichlorides of Organic Bases.] Arthur Rosenheim and Paul Frank (*Ber.*, 1905, **38**, 812—816. See this vol., ii, 256).

Bromotetrahydroquinoline. Franz Kunckell and Wilhelm Theopold (*Ber.*, 1905, **38**, 848—850).—The *hydrobromide* of *bromoacetyltetrahydroquinoline* is obtained in well-formed, yellowish-red needles melting at 125° on brominating acetyltetrahydroquinoline in glacial acetic acid. *Bromoacetyltetrahydroquinoline*, $C_{11}H_{12}ONBr$, crystallises in colourless prisms melting at 60° and yields a *platinichloride* which crystallises in dark red, cubical plates and melts at 188°. *Bromotetrahydroquinoline*, prepared by the action of 20 per cent. hydrochloric acid on the foregoing acetyl derivative, separates in colourless crystals melting at 32—35° and forms a *hydrochloride*

melting at 198°. A monobromotetrahydroquinoline has been described by Königs (Abstr., 1883, 1143), which is perhaps identical with this.

E. F. A.

Transformation of Pyrrole into Indoles. Synthesis of 4 : 7-Dimethylindole. GIUSEPPE PLANCHER and A. CARAVAGGI (*Atti R. Accad. Lincei*, 1905, [v], 14, i, 157—161).—In order to establish the constitution of the base $C_{10}H_{11}N$, melting at 101—102° and obtained by condensing pyrrole with acetonylacetone by means of zinc acetate in acetic acid solution (see Plancher, Abstr., 1902, i, 640), as that of 4 : 7-dimethylindole, the authors have synthesised it from the *p*-xylylhydrazone of pyruvic acid. On condensing this compound in presence of zinc chloride, it yields 4 : 7-dimethylindole-2-carboxylic acid, $\begin{matrix} CH:CMe\cdot C-CH \\ | \qquad\quad \| \\ CH:CMe\cdot C\cdot NH \end{matrix}\!\!>\!C\cdot CO_2H$, which partially decomposes, giving 4 : 7-dimethylindole, $\begin{matrix} CH:CMe\cdot C-CH \\ | \qquad\quad \| \\ CH:CMe\cdot C\cdot NH \end{matrix}\!\!>\!CH$, melting at 101—102°.

p-*Xylylhydrazine*, $C_8H_{12}N_2$, crystallises in colourless needles melting at 74° and undergoes rapid change when exposed to light and air. Its *hydrochloride*, $C_8H_{12}N_2,HCl$, crystallises from water in shining, white scales melting at 206°.

Pyruvic acid p-*xylylhydrazone*, $C_{11}H_{14}O_2N_2$, forms a pale yellow precipitate which melts and decomposes at 164°. The *ethyl* derivative, $C_{13}H_{18}O_2N_2$, separates from aqueous alcohol in pale yellow crystals melting at 50°.

T. H. P.

Action of Chloroform on 2 : 3-Dimethylindole. Transformation of Pyrrole into Pyridine. GIUSEPPE PLANCHER and ORESTE CARRASCO (*Atti R. Accad. Lincei*, 1905, [v], 14, i, 162—165).—The authors find that the action of chloroform on 2 : 3-dimethylindole yields, besides 2 : 3-dimethyl-3-dichloromethylindolenine (compare Abstr., 1903, i, 449), another base which can be prepared from the latter, and which is shown to be 3-chloro-2 : 4-dimethylquinoline.

2 : 3-*Dimethyl*-3-*dichloromethylindolenine picrate*,

$$C_{11}H_{11}NCl_2,C_6H_7O_7N_3,$$

separates in reddish-yellow crystals melting at 164—165°. The *oxime* of the base, $C_{11}H_{10}ON_2Cl_2$, separates from benzene in crystals melting at 203°. The *methiodide*, $C_{12}H_{14}NCl_2I$, crystallises from alcohol in slender leaflets melting and decomposing at 220—221°.

3-*Chloro*-2 : 4-*dimethylquinoline*, $C_{11}H_{10}NCl$, which can be obtained in larger quantity by heating 2 : 3-dimethyl-3-dichloromethylindolenine with sodium ethoxide at 100°, separates from aqueous alcohol in colourless, silky needles melting at 75°. The *picrate*, $C_{17}H_{13}O_7N_4Cl$, crystallises from alcohol in pale yellow prisms melting at 210°.

T. H. P.

Derivatives of *o*-Amino-*m*-xylyl-*p*-toluidine. REINHOLD VON WALTHER and R. BAMBERG (*J. pr. Chem.*, 1905, [ii], 71, 153—163. Compare Cohn and Fischer, Abstr., 1900, i, 690).—The following condensation products, $C_7H_7\cdot NH\cdot CH_2\cdot C_7H_6\cdot N:CHR$, are formed by heat-

ing *o*-amino-*m*-xylyl-*p*-toluidine [6-amino-*m*-methylbenzyltoluidine] with the corresponding aldehydes.

R = Me crystallises in slender, white needles and melts at 114°; R = Ph crystallises in white needles and melts at 125°; R = *o*-$C_6H_4 \cdot NO_2$ crystallises in sheaves of slender, orange needles and melts at 154·5°; R = *m*-$C_6H_4 \cdot NO_2$ crystallises in slender, yellow needles and melts at 132—133°; R = *p*-$C_6H_4 \cdot NO_2$ crystallises in long, orange needles and melts at 127—128°; R = *o*-$C_6H_4 \cdot OH$ crystallises in slender, yellow needles and melts at 136—137°. The action of sodium nitrite on 6-amino-*m*-methylbenzyl-*p*-toluidine in glacial acetic acid solution or of amyl nitrite on the base in alcoholic solution leads to the formation of 3-p-*tolyl*-6-*methyl*-3 : 4-*dihydro-β-phenotriazine*,

$$\begin{array}{l} CH{=}CH \cdot C \cdot N{=\!=}N \\ CMe{:}CH \cdot C \cdot CH_2 \cdot N \cdot C_7H_7 \end{array},$$

which crystallises in slender, yellow needles, melts and decomposes at 173°, and is easily soluble in hot alcohol or benzene, but only slightly so in ether or light petroleum. With cold concentrated hydrochloric acid, it forms a yellow *hydrochloride*, which gradually dissolves in the acid; the *picrate*, $C_{21}H_{18}O_7N_6$, crystallises in nodules composed of orange, monoclinic prisms and melts and decomposes at 138°; the *platinichloride*, $(C_{15}H_{15}N_3)_2,H_2PtCl_6$, crystallises in yellow, hexagonal leaflets or in prismatic plates, becomes brown at 150°, and melts at 180°. When warmed with dilute acids, the phenotriazine evolves nitrogen and yields o-*hydroxy*-m-*methylbenzyl*-p-*toluidine*, $C_7H_7 \cdot NH \cdot CH_2 \cdot C_7H_6 \cdot OH$, which dissolves in ether to a violet, fluorescent solution and forms a *picrate*, $C_{21}H_{20}O_8N_4$; this crystallises in small, transparent, yellow leaflets and melts and decomposes at 268·5°.

G. Y.

d-**Phenylamylhydrazine.** CARL NEUBERG and MAX FEDERER (*Ber.*, 1905, **38**, 866—868).—d-*Phenylamylhydrazine*,

$$CHMeEt \cdot CH_2 \cdot NPh \cdot NH_2,$$

prepared by heating *d*-amyl bromide containing 94 per cent. of the pure substance with the sodium derivative of phenylhydrazine in presence of benzene, boils at 173—175° under 50 mm. pressure, and has a sp. gr. 0·9521; when distilled immediately after being prepared, it has $[\alpha]_D + 4°45'$, but on distilling after it has been kept for 6 weeks, it has $[\alpha]_D + 6°40'$. The *hydrochloride*, $C_{11}H_{18}N_2,HCl$, forms white crystals.

W. A. D.

Resolution of Racemic Substances. II. CARL NEUBERG and MAX FEDERER (*Ber.*, 1905, **38**, 868. Compare Abstr., 1903, i, 461).—*d*-Phenylamylhydrazine (preceding abstract) gives excellent results in resolving racemic ketones and aldehydes into their optically active forms. l-*Arabinose*-d-*phenylamylhydrazone*, $C_{10}H_{14}O_6N_2$, prepared from *l*-arabinose and the hydrazine, crystallises from a mixture of alcohol and water in nodular aggregates and melts at 127°. d-*Arabinose*-d-*phenylamylhydrazone* melts at 115° and is much more soluble than the *l*-form; on this account, *i*-arabinose is easily resolved into its constituents by combining it with *d*-phenylamylhydrazine.

d-*Galactose*-d-*phenylamylhydrazone* crystallises well from a mixture of alcohol and water and melts at 127—128°. *i*-Galactose is resolved almost quantitatively into its constituents by combining it with *d*-phenylamylhydrazine.

On heating racemic acid with *d*-phenylamylhydrazine and crystallising the product from water, d-*tartaric*-d-*phenylamylhydrazide*,

$$C_2H_2(OH)_2(CO\cdot NH\cdot NPh\cdot C_5H_{11})_2,$$

melting at 206°, is obtained; on hydrolysing it with aqueous barium hydroxide, *d*-tartaric acid is separated. l-*Tartaric*-d-*phenylamylhydrazide* is easily soluble in water. W. A. D.

Diquinolyls. STEFAN VON NIEMENTOWSKI and M. SEIFERT (*Ber.*, 1905, **38**, 762—766. Compare Abstr., 1902, i, 21).—With either 2 : 2′-dinitrodiphenyl or arsenic acid as the oxidising agent, 2 : 2′-diaminodiphenyl undergoes Skraup's reaction, yielding 8 : 8′-*diquinolyl*, $C_{18}H_{12}N_2$; this crystallises in glistening, white leaflets or hexagonal plates, melts at 205—207°, is moderately soluble in hot alcohol, acetone, benzene, or carbon tetrachloride, easily so in chloroform, does not form a methiodide when heated with methyl iodide in methyl-alcoholic solution at 160° under pressure, and is nitrated only when heated with sulphuric and nitric acids at 180° in a sealed tube. The *hydrochloride*, $C_{18}H_{12}N_2,2HCl$, forms stellate groups of crystals; the *hydrobromide*, $C_{18}H_{12}N_2,2HBr$, obtained on heating the base with ethylene dibromide at 160°, forms microscopic, brown crystals; the *hydriodide*, $C_{18}H_{12}N_2,2HI$, crystallises in leaflets and long spears and melts at about 250°; the *nitrate* crystallises in white, microscopic plates and melts and decomposes at 210—230°; the *sulphate*, $C_{18}H_{12}N_2,H_2SO_4,H_2O$, forms white crystals; the *aurichloride*, $C_{18}H_{12}N_2,2HAuCl_4$, crystallises in golden needles and melts and decomposes at 285°; the *platinichloride*, $C_{18}H_{12}N_2,H_2PtCl_6$, is obtained as a yellow precipitate.

5 : 5′-*Dimethyl*-8 : 8′-*diquinolyl*, $C_{20}H_{16}N_2$, prepared by Skraup's reaction from 2 : 2′-diamino-4 : 4′-dimethyldiphenyl with arsenic acid as the oxidising agent, crystallises in yellow, tree-like aggregates of needles and leaflets, melts at 215°, is easily soluble in hot alcohol, acetone, chloroform, or benzene, and in its resistance to chemical reagents resembles diquinolyl. The *hydrochloride*, $C_{20}H_{16}N_2,2HCl$, crystallises in microscopic, white needles and melts and decomposes at about 320°; the *nitrate*, $C_{20}H_{16}N_2,2HNO_3$, crystallises in long, yellow spears and decomposes at 210°. G. Y.

Influence of the Position of Methyl and Nitro-groups relatively to the Methane Carbon Atom on the Colours of Triphenylmethane Dyes. FRITZ REITZENSTEIN and OTTO RUNGE (*J. pr. Chem.*, 1905, [ii], **71**, 57—132. Compare Abstr., 1904, i, 804; Nölting, Abstr., 1892, 187).—The introduction of methyl groups into hexa-alkyltriaminotriphenylmethane dyes in the meta-positions to the dialkylamino-groups is accompanied by a change in the colour from violet to blue, and finally to green, the colour changing with the increasing number of methyl-*m*-dialkylamino-groupings. The dark green colour of the 3 : 4′ : 4″-hexamethyltriaminotriphenylmethane changes to a pure bluish-green in the dye of 3 : 4′ : 4″-hexamethyltriamino-

6-methyltriphenylmethane, but, on the further introduction of methyl groups to form the tri-*o*-tolylmethane dye, the colour is merely weakened; this is due to the simultaneous presence of methyl-*m*-dialkylamino- and methyl-*p*-dialkylamino-systems, which neutralise each other.

The introduction of a nitro-group into the ortho-position of hexa-alkyltriaminotriphenylmethane dyes results in a change from dark to light green; if the nitro-group assumes the meta-position, the colour of the dye is weakened, whilst the reddish-blue of the 2 : 4′ : 4″-hexamethyltriamino-5-methyltriphenylmethane dye becomes a pure blue in the *p*-nitro-derivative. This tendency to change from green to blue on introduction of a nitro-group is not displayed by the dyes derived from tetramethyldiaminoditolylhydrol.

The leuco-base, formed by condensation of tetramethyldiaminobenzhydrol and aniline in presence of hydrochloric acid, melts at 65° and consists of a mixture of *p*-amino- with a small quantity of *o*-aminoleucomalachite-green; that obtained by condensation in presence of concentrated sulphuric acid melts at 60° and is a mixture of *o*-, *m*-, and *p*-aminoleucomalachite-greens (compare Nathanson and Müller, Abstr., 1889, 1188).

As has been shown by Nölting, the condensation of tetramethyldiaminobenzhydrols with aromatic bases leads to the formation of isomeric leuco-bases, the nature of the product depending on whether hydrochloric or sulphuric acid is used as the condensing agent; this also holds good for condensations with tetramethyldiaminoditolylhydrol.

Amongst others, the following new leuco-bases have been prepared by the condensation of tetramethyldiaminobenzhydrol with aromatic bases in presence of hydrochloric acid.

4-*Amino*-4′ : 4″-*tetramethyldiamino*-2-*methyltriphenylmethane*, from *m*-toluidine, is a blue powder, melts at 224—225°, and yields a blue dye. 4′ : 4″-*Tetramethyldiamino*-2-*ethylamino*-5-*methyltriphenylmethane*, from ethyl-*p*-toluidine, is a white powder; the dye fixed with tartaric and tannic acids colours cotton-wool blue. 2 : 4′ : 4″-*Hexamethyltriamino*-5-*methyltriphenylmethane*, from dimethyl-*p*-toluidine, is precipitated by ammonia as a white powder, which on filtration becomes a tar; the dye colours tannin mordanted cotton-wool blue.

4-*Amino*-4′ : 4″-*tetramethyldiamino*-2 : 3-*dimethyltriphenylmethane*, from *o*-xylidine, forms nodular crystals and melts and decomposes at 168°; the *dye* colours tannin mordanted cotton-wool an intense blue.

The following leuco-bases, which have not been previously described, have been prepared by the condensation of tetramethyldiaminobenzhydrol with aromatic bases in presence of concentrated sulphuric acid.

3-*Methylamino*-4′ : 4″-*tetramethyldiamino*-4-*methyltriphenylmethane*, from methyl-*o*-toluidine, forms a light blue powder; the *dye* colours tannin mordanted cotton-wool green. 3-*Amino*-4′ : 4″-*tetramethyldiamino*-5-*methyltriphenylmethane*, from *m*-toluidine, is a blue powder; the *dye* colours tannin mordanted cotton-wool blue. 4′ : 4″-*Tetramethyldiamino*-3-*ethylamino*-6-*methyltriphenylmethane*, from ethyl-*p*-toluidine, is a light blue powder; the *dye* colours tannin mordanted cotton-wool a bluish-green. 3 : 4′ : 4″-*Hexamethyltriamino*-5-*methyltriphenylmethane*,

from dimethyl-*m*-toluidine, is obtained as a green, flocculent precipitate; the dye colours tannin mordanted cotton-wool blue.

4′ : 4″-*Tetramethyldiamino-3-diethylamino-5-methyltriphenylmethane*, from diethyl-*m*-toluidine, forms a brown powder and melts on the water-bath; the zinc chloride salt of the dye forms glistening, bronze crystals and dyes cotton wool an intense blue.

In presence of hydrochloric acid, tetraethyldiaminobenzhydrol condenses with diethyl-*m*-toluidine to form 4 : 4′ : 4″-*hexaethyltriamino-2-methyltriphenylmethane*, which is brown; the zinc chloride salt of the dye forms brown, glistening crystals and colours mordanted cotton-wool blue. The dye obtained on oxidation of the base formed by the condensation of tetraethyldiaminobenzhydrol and dimethyl-*m*-toluidine in presence of concentrated sulphuric acid forms a reddish-brown, crystalline double salt with zinc chloride and colours mordanted cotton-wool blue. The zinc chloride salt of the dye, obtained on oxidation of the condensation product of tetraethyldiaminobenzhydrol with diethyl-*p*-toluidine in presence of concentrated sulphuric acid forms glistening, bronze crystals and colours mordanted cotton-wool blue.

pp-*Tetramethyldiaminodi*-o-*tolylmethane*, $CH_2(C_6H_3Me{\cdot}NMe_2)_2$, prepared by acting on dimethyl-*m*-toluidine with formaldehyde in alcoholic hydrochloric acid solution or in concentrated hydrochloric acid, crystallises in white, glistening leaflets, melts at 82°, and is converted into tetramethyldiaminodi-*o*-tolylhydrol by oxidation with lead peroxide in dilute acetic acid solution or electrolytically between lead electrodes in dilute sulphuric acid solution.

pp-*Tetramethyldiaminodi*-o-*tolylhydrol*, $CH(C_6H_3Me{\cdot}NMe_2)_2{\cdot}OH$, is also formed by electrolytic reduction of the corresponding ketone between lead electrodes in dilute sulphuric acid solution; it is obtained as a white powder, which becomes brown on exposure to air and melts at about 50°. pp-*Tetramethyldiaminodi*-o-*tolyl ketone* is formed by the action of phosgene on dimethyl-*m*-toluidine at 100—150°; after removal of the excess of dimethyl-*m*-toluidine by a current of steam, the ketone is precipitated as the green, resinous substance on addition of sodium hydroxide.

Tetramethyldiaminoditolylhydrol condenses with aniline to form a mixture of leuco-bases; in the presence of concentrated sulphuric acid, the product is a light blue powder, which on oxidation yields an earthy-blue dye; the product, obtained in presence of hydrochloric acid, is a blue powder and yields a dull blue dye. With dimethylaniline in concentrated sulphuric acid, tetramethyldiaminoditolylhydrol forms a light brown powder, which melts at 85°, and on oxidation yields a dye, which dyes mordanted cotton-wool a dull blue.

The following leuco-bases were obtained by condensation of tetramethyldiaminoditolylhydrol with aromatic bases in presence of hydrochloric acid.

4-*Amino*-4′ : 4″-*tetramethyldiamino*-3 : 2′ : 2″-*trimethyltriphenylmethane*, from *o*-toluidine, is a light grey powder, yields a blue *dye*, and, on diazotisation, is converted into *tetramethyldiaminotritolylmethane*, which on oxidation yields a weak bluish-green *dye*.

2-*Amino*-4′ : 4″-*tetramethylamino*-2′ : 2″ : 5-*trimethyltriphenylmethane*,

from *p*-toluidine, sinters at about 62°, melts indefinitely at a higher temperature, and yields a greenish-blue *dye*. 4′ : 4″-*Tetramethyldiamino-2-ethylamino-2′ : 2″ : 5-trimethyltriphenylmethane*, from ethyl-*p*-toluidine, is obtained as a reddish-brown powder, which yields a bluish-green *dye* on oxidation. 4′ : 4″-*Hexamethyltriamino-2′ : 2″ : 3-trimethyltriphenylmethane*, from dimethyl-*o*-toluidine, crystallises from alcohol in white flakes, and, after oxidation, dyes mordanted cotton-wool a light blue. 2 : 4′ : 4″-*Hexamethyltriamino 2′ : 2″ : 5-trimethyltriphenylmethane*, from dimethyl-*p*-toluidine, becomes blue on oxidation. 4-*Amino*-4′ : 4″-*tetramethyldiamino*-2 : 2′ : 2″ : 3-*tetramethyltriphenylmethane*, from *o*-xylidine, crystallises from toluene and yields a bluish-green solution on oxidation. 2-*Amino*-4′ : 4″-*tetramethyldiamino*-2′ : 2″ : 3 : 5-*tetramethyltriphenylmethane*, from *m*-xylidine, is reddish-brown and becomes light green on oxidation. 4 - *Amino* - 4′ : 4″ - *tetramethyldiamino*-2 : 2′ : 2″ : 5 - *tetramethyltriphenylmethane*, from *p*-xylidine, separates from a mixture of benzene and petroleum in olive-green crystals and yields a green dye solution on oxidation.

The following leuco-bases were formed by the condensation of tetramethyldiaminoditolylhydrol with the aromatic bases named in concentrated sulphuric acid.

3-*Amino*-4′ : 4″-*tetramethyldiamino*-2′ : 2″ : 4-*trimethyltriphenylmethane*, from *o*-toluidine, melts at 120°, is oxidised to a weak bluish-green dye, and, on diazotisation, yields 4′ : 4″-*tetramethyldiamino*-2′ : 2″ : 3-*trimethyltriphenylmethane*, which is obtained as a yellow, granular powder. 3-*Amino*-4′ : 4″-*tetramethyldiamino*-2′ : 2″ : 5-*trimethyltriphenylmethane*, from *m*-toluidine, yields a weak blue dye solution. 5-*Amino*-4′ : 4″-*tetramethyldiamino*-2 : 2′ : 2″-*trimethyltriphenylmethane*, from *p*-toluidine, yields a green dye solution, and, on diazotisation, is converted into 4′ : 4″-*tetramethyldiamino*-2 : 2′ : 2″-*trimethyltriphenylmethane*, which is obtained as a yellow powder, becoming bluish-green on oxidation. 4′ : 4″-*Tetramethyldiamino - 5 - ethylamino - 2 : 2′ : 2″ - trimethyltriphenylmethane*, from ethyl-*p*-toluidine, is obtained as a grey precipitate, which becomes green on oxidation. 3 : 4′ : 4″-*Hexamethyltriamino*-2′ : 2″ : 4-*trimethyltriphenylmethane*, from dimethyl-*o*-toluidine, melts after sintering at 98°, and, when oxidised, dyes mordanted cotton-wool a weak green. 3 : 4′ : 4″-*Hexamethyltriamino*-2′ : 2″ : 5-*trimethyltriphenylmethane*, from dimethyl-*m*-toluidine, is obtained as a grey precipitate on addition of light petroleum to its solution in benzene, and forms a light blue solution when oxidised. 4′ : 4″ : 5-*Hexamethyltriamino*-2 : 2′ : 2″-*trimethyltriphenylmethane*, from dimethyl-*p*-toluidine, crystallises from a mixture of benzene and light petroleum, and, after oxidation, dyes tannin mordanted cotton a weak bluish-green. 3-*Amino*-4′ : 4″-*tetramethyldiamino*-2′ : 2″ : 4 : 5-*tetramethyltriphenylmethane*, from *o*-xylidine, separates from a mixture of benzene and light petroleum in grey crystals, and on oxidation yields a brown solution, which has no dyeing properties. 5-*Amino*-4′ : 4″-*tetramethyldiamino*-2 : 2′ : 2″ : 4-*tetramethyltriphenylmethane*, from *m*-xylidine, separates from a mixture of toluene and light petroleum in grey crystals, and, on oxidation, yields a weak brown *dye*. 3-*Amino*-4′ : 4″-*tetramethyldiamino*-2 : 2′ : 2″ : 5-*tetramethyltriphenylmethane*, from *p*-xylidine, is light blue, and on oxidation yields a brown solution.

In hydrochloric acid, tetramethyldiaminobenzhydrol condenses with *o*-nitro-*p*-toluidine to form 4-*nitro*-2-*amino*-4′ : 4″-*tetramethyldiamino*-5-*methyltriphenylmethane*, which is obtained as a resin, and, when oxidised, dyes tannin mordanted cotton-wool an intense blue. In concentrated sulphuric acid, the condensation leads to the formation of 5-*nitro*-3-*amino*-4′ : 4″-*tetramethyldiamino*-6-*methyltriphenylmethane*, which is obtained as a green substance ; the dye solution colours mordanted cotton-wool a light bluish-green. In hydrochloric acid, the hydrol condenses with *p*-nitro-*o*-toluidine to form 5-nitro-2-amino-4′ : 4″-tetramethyldiamino-3-methyltriphenylmethane, which is obtained as a green powder, and, after oxidation, colours mordanted cotton-wool a dark blue. In concentrated sulphuric acid, the condensation with *p*-nitro-*o*-toluidine leads to the formation of 6-*nitro*-3-*amino*-4′ : 4″-*tetramethyldiamino*-4-*methyltriphenylmethane*, which, after oxidation, dyes tannin mordanted cotton-wool a light bluish-green. With *o*-nitrodimethyl-*p*-toluidine in hydrochloric acid, the benzhydrol condenses to 4-*nitro*-2 : 4′ : 4″-*hexamethyltriamino*-5-*methyltriphenylmethane*, which is obtained as a resin ; the *dye* colours tannin mordanted cotton-wool an intense blue. In concentrated sulphuric acid, this condensation leads to the formation of 5-*nitro*-3 : 4′ : 4″-*hexamethyltriamino*-6-*methyltriphenylmethane*, which is obtained as a resin ; the *dye* solution colours tannin mordanted cotton-wool green. In hydrochloric acid, the benzhydrol condenses with *p*-nitrodimethyl-*o*-toluidine to form 5-*nitro* 2 : 4′ : 4″-*hexamethyltriamino*-3-*methyltriphenylmethane*, which, after oxidation, dyes mordanted cotton-wool an intense blue. In concentrated sulphuric acid, this condensation leads to the formation of 6-*nitro*-3 : 4′ : 4″-*hexamethyltriamino*-4-*methyltriphenylmethane*, which, after oxidation, dyes tannin mordanted cotton-wool a light green.

Tetramethyldiaminoditolylhydrol condenses slowly with *o*-nitro-*p*-toluidine to form 5-*nitro*-3-*amino*-4′ : 4″-*tetramethyldiamino*-2′ : 2″ : 6-*trimethyltriphenylmethane* ; the yellowish-brown leuco-base, on oxidation, yields a brown solution. 4-*Nitro*-2-*amino*-4′ : 4″-*tetramethyldiamino*-2′ : 2″ : 5-*trimethyltriphenylmethane*, obtained by this condensation in hydrochloric acid, is an olive-green substance, which, on oxidation, yields a bluish-green dye solution. With *p*-nitro-*o*-toluidine in concentrated sulphuric acid, the ditolylhydrol condenses to 6-*nitro*-3-*amino*-4′ : 4″-*tetramethyldiamino*-2′ : 2″ : 4-*trimethyltriphenylmethane* ; the yellowish-brown leuco-base, on oxidation, yields a brown solution. 6-Nitro-4-amino-4′ : 4″-tetramethyldiamino-2′ : 2″ : 3-trimethyltriphenylmethane, formed by the condensation with *p*-nitro-*o*-toluidine in hydrochloric acid, is an olive-green substance, which, on oxidation, yields a bluish-green dye solution.

When boiled with 1-chloro-2 : 4-dinitrobenzene and sodium acetate in absolute alcoholic solution in a reflux apparatus, the leuco-base obtained by condensation of tetramethyldiaminobenzhydrol and aniline in presence of concentrated sulphuric acid yields a *dinitroanilino*-leuco-base, which is a dark red powder and melts at about 154° ; an orange-coloured *substance* melting at 171° crystallises slowly from the alcoholic mother liquor. A similar reddish-brown *dinitroanilino*-leuco-base is obtained from the hydrochloric acid condensation product of tetramethyldiaminobenzhydrol and aniline ; these leuco-bases, when dis-

solved in hydrochloric acid, colour tannin mordanted cotton-wool yellow, and gelatinise when oxidised with lead peroxide. The *dinitroanilino-leuco-base*, obtained from the sulphuric acid condensation product of tetramethyldiaminoditolylhydrol and aniline, is a brownish-red substance, which, after oxidation, dyes tannin mordanted cotton-wool a weak earthy-green. The dye solution, obtained in the same manner from the hydrochloric acid condensation product of the ditolylhydrol and aniline, is a weak blue.

The following dinitroanilino-leuco-bases are prepared in the same manner from the corresponding leuco-bases.

o-*Dinitroanilinoleucomalachite-green*, is a yellow substance which in hydrochloric acid solution dyes tannin mordanted cotton-wool yellow and gelatinises on oxidation. 3-*Dinitroanilinoleucomalachite-green* is a cochineal-coloured substance, which dyes tannin mordanted cotton-wool yellow in hydrochloric acid solution and yields a *dye*, which forms glistening, red crystals and colours tannin mordanted cotton-wool a yellowish-green. 4-*Dinitroanilinoleucomalachite green* is a yellowish-brown substance, which dyes tannin mordanted cotton-wool a weak sulphur-yellow, and gelatinises when oxidised. 4′ : 4″-*Tetramethyldiamino*-3-*dinitroanilino*-4-*methyltriphenylmethane* is a reddish-brown substance, which, when oxidised, yields a green dye. 4′ : 4″-*Tetramethyldiamino*-3-*dinitroanilino*-5-*methyltriphenylmethane* is a yellowish-brown substance, melts at 200—201°, dyes tannin mordanted cotton-wool a lemon-yellow in hydrochloric acid solution, and is oxidised by lead peroxide to an intense earthy-green ; when reduced with zinc dust in dilute hydrochloric acid solution, the leuco-base yields a brown *product*, which, when oxidised, dyes tannin mordanted cotton-wool steel-blue. 4′ : 4″-*Tetramethyldiamino*-3-*dinitroanilino*-6-*methyltriphenylmethane* is a dark red substance, which, when oxidised, yields an intense green dye and is reduced by zinc dust in hydrochloric acid solution to the aminonitrophenyl *derivative* ; this brown leuco-base yields on oxidation an intense bluish-green dye. 4′ : 4″-*Tetramethyldiamino*-3-*dinitrophenylethylamino*-6-*methyltriphenylmethane* is a reddish-brown substance, which yields an intense green dye. 4′ : 4″-*Tetramethyldiamino*-4-*dinitroanilino*-2-*methyltriphenylmethane* is reddish-brown, melts at 197°, and is oxidised to an intense earthy-green dye. 4′ : 4″-*Tetramethyldiamino*-2-*dinitroanilino*-2′ : 2″-*dimethyltriphenyl methane* is reddish-brown and yields a dye solution, which colours tannin mordanted cotton-wool a dirty green. 4′ : 4″-*Tetramethyldiamino*-3-*dinitroanilino*-2′ : 2″-*dimethyltriphenylmethane* is reddish-brown and yields, on oxidation, a weak green dye solution. 4′ : 4″-*Tetramethyldiamino*-4-*dinitroanilino*-2′ : 2″-*dimethyltriphenylmethane* is a brown powder ; the dye solution is a dull green. 4′ : 4″-*Tetramethyldiamino*-3-*dinitroanilino*-2′ : 2″ : 6-*trimethyltriphenylmethane* is yellow, and on oxidation yields a dye solution which colours tannin mordanted cotton-wool yellowish-green.

The acetyl and *p*-toluenesulphonyl derivatives of *m*-aminoleucobases were found to yield green dye solutions. G. Y.

New Reaction of Semicarbazones. III. Preparation of the Hydrazides of Aromatic Substituted Carbamic Acids from Semicarbazide. WALTHER BORSCHE (*Ber.*, 1905, 38, 831—837. Compare Abstr., 1902, i, 186).—Phenylcarbamic hydrazide hydro-

chloride and similar compounds are conveniently prepared by heating acetone or acetophenone semicarbazone with aniline and subsequently decomposing the hydrazone formed by heating with hydrochloric acid. *Ethyl acetophenonecarboxylatehydrazone* crystallises in colourless needles which melt at 119—120°; on heating with aniline, it forms *acetophenonephenylcarbamic acid hydrazone,* melting at 187—188°, and crystallises in colourless needles. p-*Tolylcarbamic hydrazide* crystallises in colourless plates melting at 259—260°, the *hydrochloride* forms colourless, silky, glistening needles melting at 242°. It yields hydrazone derivatives with aldehydes and ketones; *acetone*-p-*tolylcarbamic hydrazone,* $CMe_2:N\cdot NH\cdot CO\cdot NH\cdot C_7H_7$, separates in needles aggregated in clusters and melts at 174—175°; the corresponding *acetophenone* compound, $CMePh:N\cdot NH\cdot CO\cdot NH\cdot C_7H_7$, melts at 192° and the *o*-hydroxybenzylidene-*p*-tolylcarbamic hydrazone,

$$OH\cdot C_6H_4\cdot CH:N\cdot NH\cdot CO\cdot NH\cdot C_7H_7,$$

at 238—239°. p-*Hydroxybenzeneazoformo*-p-*toluidide,*

$$OH\cdot C_6H_4\cdot N:N\cdot CO\cdot NH\cdot C_7H_7,$$

forms small, red crystals melting at 173—174°.

o-*Tolylcarbamic hydrazide* melts at 142—143°; the *hydrochloride* separates in silvery, glistening needles and plates or in colourless cubes and melts at 184—186°; the acetonehydrazone melts at 156°, the acetophenonehydrazone at 211—212°, and the *o*-hydroxybenzylidene derivative at 204·5°, whilst the dark red crystals of o-*hydroxybenzeneazoformo*-o-*toluidide* melt at 164—165°.

β-Naphthylcarbamic hydrazide forms a colourless powder melting at 258—259°; the *hydrochloride* decomposes at 230° and is completely melted at 260°. The *acetophenone* derivative melts at 201—202°, the o-*hydroxybenzylidene* derivative at 251—252°, and p-*hydroxybenzeneazoformo-β-naphthylamide* at 189—190°. E. F. A.

The Presence and Action of Mercaptan Groups in Direct Sulphur Dyes. RAYMOND VIDAL (*Chem. Centr.*, 1905, i, 411—412; from *Mon. scient.*, [iv], 19, i, 25).—The solubility of the sulphur dyes in alkali sulphides is not necessarily due to mercaptan groups, but may result from the presence of phenolic groups.

When *p*-aminophenol is melted with sulphur in sufficient quantity to form the thiazine, a bluish-black dye soluble in cold sodium sulphide is formed. When heated with sodium sulphide, a blue or bluish-black colour assumes a greenish shade the more readily when few substituents are present, that is, when the chances of the introduction of mercaptan groups, to which the colour change is due, are greatest. Substituents do not exercise so great an influence on the shade as the proportions of materials and the temperature used in the preparation. The author explains the formation of Vidal-black from *p*-aminophenol and sulphur by the production of the compound

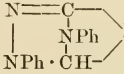
$$OH\cdot C_6H_3<\begin{smallmatrix}NH\\ S\end{smallmatrix}>C_6H_3\cdot NH_2,$$

two molecules of which with sulphur then give

$$OH\cdot C_6H_3<\begin{smallmatrix}NH\\ S\end{smallmatrix}>C_6H_2<\begin{smallmatrix}S\\ NH\end{smallmatrix}>C_6H_2<\begin{smallmatrix}NH\\ S\end{smallmatrix}>C_6H_3\cdot OH.$$

G. D. L.

*endo*Iminotriazoles. MAX BUSCH (*Ber.*, 1905, **38**, 856—860).—Trialkylaminoguanidines of the type NHR′·C(NHR″):N·NHR are readily prepared by the interaction of carbodiphenylimides with alkylhydrazines; this method of preparation was attempted by Wessel (Abstr., 1888, 1083), but without success owing to the action having been allowed to go too far. Triphenylaminoguanidine, $C(NHPh)_2$:N·NHPh, is prepared by heating thiocarbanilide with mercuric oxide and benzene, removing the precipitated mercuric sulphide, and adding phenylhydrazine to the hot filtrate.

1 : 4-*Diphenyl*-3 : 5-endo*anilodihydrotriazole*,  , obtained by heating triphenylaminoguanidine with formic acid at 175°, crystallises from alcohol in highly lustrous, yellow leaflets or plates and melts and decomposes at 189°; it resists the action of acids, but is easily hydrolysed by alcoholic potassium hydroxide initially into its constituents, the triphenylaminoguanidine then being oxidised to benzeneazoanilinophenyliminomethane, NPh:N·C(NHPh):NPh. *Diphenylendoanilodihydrotriazole nitrate*, $C_{20}H_{16}N_4,HNO_3$, is extraordinarily sparingly soluble in water (compare this vol., ii, 283); the *sulphate*, $C_{20}H_{16}N_4,H_2SO_4$, melts at 100—101°, and the *hydrochloride* at 242°. Formic acid gives rise to two *salts*: (1) $C_{20}H_{16}N_4,CH_2O_2$ melts and decomposes at 168°; (2) $C_{20}H_{16}N_4,2CH_2O_2$ forms large, lustrous needles and melts and decomposes at 128°. The following salts also form good crystals: the *hydriodide, perchlorate, bromate, sulphite*, and *cyanate*.

W. A. D.

Decomposition of *o*-Nitrobenzyl Alcohol under the Influence of Aqueous and of Alcoholic Sodium Hydroxide. PAUL CARRÉ (*Compt. rend.*, 1905, **140**, 663—665. Compare Freundler, Abstr., 1904, i, 667).—When *o*-nitrobenzyl alcohol is warmed with aqueous sodium hydroxide, the chief products are anthranilic acid, *o*-azobenzoic acid, and o-*benzaldehyde*-o-*azobenzoic acid*,

$$CHO·C_6H_4·N_2·C_6H_4·CO_2H.$$

The aldehyde acid was not isolated, but its *oxime*, which crystallises from acetic acid in orange spangles melting at 232°, and its *semicarbazone*, which forms orange needles melting at 240°, were obtained. The aldehyde acid changes, slowly in the cold, rapidly on warming, into a pale yellow compound melting at 294°, which is represented by the formula $(C_{14}H_8N_2O_2)_2$.

In smaller quantities, *o*-nitrobenzaldehyde and *o*-aminobenzaldehyde are produced. The former gives a *p*-nitrophenylhydrazone in the form of small, red prisms which melt at 263°. The chloride of the latter gives a double chloride with mercury of the formula

$$2COH·C_6H_4·NH_2,HCl,3HgCl_2;$$

this crystallises from water in needle-shaped crystals melting at 149°.

There were no indications of the formation of azoxybenzoic acid or of nitrotoluene, which is contrary to the statements of Jaffé (*Zeit. physiol. Chem.*, 1878, **2**, 55).

When acted on by alcoholic soda, the principal products are *o*-indazyl-

benzoic acid and benzaldehyde *o*-azobenzoic acid. In smaller quantities, *o*-aminobenzyl alcohol, *o*-indazylbenzyl alcohol, *o*-aminobenzaldehyde, anthranil, and anthranilic acid are obtained. Sodium ethoxide acts on the *o*-nitrobenzyl alcohol in a similar manner, but the proportion of the alcohol group which is unaltered is greater in this case. H. M. D.

Action of Cuprous Chloride on Aryldiazonium Salts. FRITZ ULLMANN and L. FRENTZEL (*Ber.*, 1905, **38**, 725—729. Compare Abstr., 1902, i, 89).—The action of cuprous chloride on *m*-nitrobenzenediazonium sulphate leads to the formation of a small quantity of *m*-chloronitrobenzene together with a much larger quantity of 3 : 3′-dinitrodiphenyl (87 per cent.). In the same manner, about equal quantities of *p*-chloronitrobenzene and 4 : 4′-dinitrodiphenyl were obtained from *p*-nitroaniline.

The following new substances were obtained by this method:

2 : 2′-*Dinitrodiphenyl*-4 : 4′-*disulphonic acid* is obtained as a brown mass from diazotised 2-nitroaniline-4-sulphonic acid; the *potassium* salt, $C_{12}H_6O_{10}N_2S_2K_2$, crystallises in yellow leaflets. 3 : 3′-*Dinitro*-4 : 4′-*ditolyl*, $C_{14}H_{12}O_4N_2$, obtained along with *p*-chloro-*o*-nitrotoluene from *o*-nitro-*p*-toluidine, separates from glacial acetic acid in brown crystals, melts at 175·5°, and is easily soluble in boiling benzene. 6 : 6′-*Dinitro*-2 : 2′-*ditolyl*, obtained along with *o*-chloro-*m*-nitrotoluene from *m*-nitro-*o*-toluidine or by heating *o*-chloro-*m*-nitrotoluene with copper powder, crystallises in small, yellow needles, melts at 110°, and is easily soluble in alcohol or benzene. 5 : 5′-*Dinitro*-2 : 2′-*ditolyl*, obtained along with 5 : 5′-dinitro-2 : 2′-azotoluene and *o*-chloro-*p*-nitrotoluene from *p*-nitro-*o*-toluidine, crystallises in yellow needles, melts at 173°, and is easily soluble in glacial acetic acid or benzene. 5 : 5′-*Dinitro*-2 : 2′-*azotoluene*, $C_{14}H_{12}O_4N_4$, crystallises in red needles, melts at 273°, and is only slightly soluble in boiling alcohol, benzene, or toluene. 4 : 4′-*Dinitro*-2 : 2′-*ditolyl*, obtained along with 2-chloro-5-nitrotoluene and 4 : 4′-dinitro-2 : 2′-azotoluene from 5-nitro-2-toluidine, crystallises in yellow leaflets, melts at 170°, and is easily soluble in boiling benzene or glacial acetic acid.

4 : 4′-*Dinitro*-2 : 2′-*azotoluene* crystallises in reddish-brown leaflets, melts at 258°, and is easily soluble in benzene, glacial acetic acid, or nitrobenzene. G. Y.

***o*-Aminoazo-dyes.** MAX BUSCH and ED. BERGMANN (*Zeit. Farb. Text. Ind.*, 1905, **4**, 105—113).—The following experiments show that *o*-aminoazo-derivatives have a normal constitution, but that they readily undergo transformation into the isodynamic form, $NH{:}C_6H_4{:}N{\cdot}NHR$, becoming thus susceptible to the so-called ortho-transformations.

o-Aminoazo-*p*-toluene readily condenses with benzenesulphonic chloride dissolved in benzene solution containing pyridine to form *benzenesulphonamino-*o*-azo-*p*-toluene*, $SO_2Ph{\cdot}NH{\cdot}C_6H_3Me{\cdot}N{:}N{\cdot}C_6H_4Me$, which crystallises from alcohol in yellow needles and melts at 155°; it does not dissolve in aqueous alkalis, but with alcoholic sodium hydroxide gives rise to a *sodium* derivative which remains dissolved

on diluting with water. The analogous benzenesulphonamino-*p*-azotoluene, on the other hand, is soluble in aqueous sodium hydroxide.

o-Benzeneazo-β-naphthylamine combines in similar manner with benzenesulphonic chloride forming the *compound*

$$SO_2Ph\cdot NH\cdot C_{10}H_6\cdot N{:}NPh,$$

which crystallises from alcohol in slender, red needles and melts at 167°.

On heating *o*-aminoazo-*p*-toluene with benzyl chloride and alcoholic sodium hydroxide, *benzylaminoazo*-p-*toluene*,

$$CH_2Ph\cdot NH\cdot C_6H_3Me\cdot N{:}N\cdot C_6H_4Me,$$

is obtained; it crystallises from a mixture of alcohol and ether in bright red needles or prisms, melts at 75°, gives a brownish-yellow crystalline *hydrochloride*, and combines with sodium nitrite, giving the *nitrosoamine*, $CH_2Ph\cdot N(NO)\cdot C_6H_3Me\cdot N_2\cdot C_6H_4Me$, which crystallises from alcohol in yellow needles melting at 116°.

On oxidising benzylaminoazo-*p*-toluene in acetone solution with potassium permanganate, the *benzylidene* compound,

$$CHPh{:}N\cdot C_6H_3Me\cdot N_2\cdot C_6H_3Me,$$

is obtained; on warming this with glacial acetic acid, it is transformed into phenyl-*p*-tolyldihydro-*p*-tolutriazine,

$$C_6H_3Me\genfrac{}{}{0pt}{}{\lessgtr N\cdot CHPh}{\quad N\cdot N\cdot C_6H_4Me}$$

(Goldschmidt and Rosell, Abstr., 1890, 614), which melts at 227° instead of 220° as formerly stated.

p-Aminoazobenzene combines with phenylthiocarbimide to form *p*-phenylthiocarbamidoazobenzene, $N_2Ph\cdot C_6H_4\cdot NH\cdot CS\cdot NHPh$, which differs from the analogous derivative formed from *o*-aminoazobenzene by not losing hydrogen sulphide when treated with mercuric oxide; it is converted instead into *p*-phenylcarbamidoazobenzene.

o-Aminoazotoluene and methylthiocarbimide give *methylthiocarbamidoazotoluene*, $NHMe\cdot CS\cdot NH\cdot C_6H_3Me\cdot N_2\cdot C_6H_4Me$, which crystallises from alcohol in thick needles and melts at 154—155°; it differs from the corresponding derivative prepared from phenylcarbimide by not being changed by boiling glacial acetic acid, and mercuric oxide in benzene fails also to convert it into a triazine derivative.

2-o-*Tolylthiocarbamidoazo*-p-*toluene*,

$$C_6H_4Me\cdot NH\cdot CS\cdot NH\cdot C_6H_3Me\cdot N_2\cdot C_6H_3Me,$$

prepared from *o*-aminoazo-*p*-toluene and *o*-tolylthiocarbimide, crystallises from alcohol in brownish-yellow leaflets, melts at 157°, and is easily transformed by glacial acetic acid into o-*tolylimino*-p-*tolyl*-p-*tolutriazine*, $C_6H_3Me\genfrac{}{}{0pt}{}{\lessgtr N\cdot C{:}N\cdot C_6H_4Me(o)}{\quad N\cdot N\cdot C_6H_4Me(p)}$, which crystallises from a mixture of ether and light petroleum in bluish-black needles and melts at 167°.

2-m-*Nitrophenylthiocarbamidoazo*-p-*toluene*, prepared from *o*-aminoazotoluene and *m*-nitrophenylthiocarbimide, forms yellowish-brown leaflets, melts at 164°, and is converted by mercuric oxide into m-*nitrophenyliminotolyltolutriazine*, $C_6H_3Me\genfrac{}{}{0pt}{}{\lessgtr N\cdot C{:}N\cdot C_6H_4\cdot NO_2}{\quad N\cdot N\cdot C_6H_4Me}$, which forms dark grey, felted needles and decomposes at about 185—190°.

Phenylazo-β-naphthylamine does not give a thiocarbamido-derivative with phenylthiocarbimide, but on heating the two substances with benzene and mercuric oxide, *phenyliminophenylnaphthatriazine*, $C_{10}H_6<\begin{matrix}N\cdot NPh\\ N\cdot C:NPh\end{matrix}$, is obtained; it crystallises from alcohol in bluish-black needles, and from a mixture of benzene or light petroleum in thick, brownish-yellow, transparent leaflets, melts at 166°, and gives a *hydrochloride*, $C_{23}H_{16}N_4,HCl$, crystallising in bright red aggregates and melting at 248°; the *nitrate* is very sparingly soluble in water.

2-*Benzeneazo*-4-*bromo*-1-*naphthylamine*, $NH_2\cdot C_{10}H_5Br\cdot N_2Ph$, obtained from 4-bromo-1-naphthylamine and benzenediazonium chloride, crystallises from alcohol in brownish-red needles and melts at 146°; the *hydrochloride* melts at 195°. In alcoholic solutions, the azo-compound combines slowly with phenylcarbimide, forming *phenyliminophenylbromonaphthatriazine*, $C_{10}H_5Br<\begin{matrix}N\cdot C:NPh\\ N\cdot NPh\end{matrix}$, which crystallises from alcohol in lustrous, blue needles, melts at 189°, and gives a yellow, crystalline *hydrochloride*.

Benzeneazo-4-*ethoxy*-1-*naphthylamine*, prepared from 1-amino-4-ethoxynaphthalene, crystallises from alcohol in red, silky needles, melts at 142°, and combines readily with phenylthiocarbimide to form *phenyliminophenyl*-4-*ethoxynaphthatriazine*, $OEt\cdot C_{10}H_5<\begin{matrix}N\cdot C:NPh\\ N\cdot NPh\end{matrix}$, which separates from xylene in lustrous, blue crystals and melts at 230°; the *hydrochloride*, $C_{25}H_{20}ON_4,1\frac{1}{2}HCl$, is abnormal, and the *picrate* melts at 195°. On reduction with hydrogen sulphide, the triazine gives *phenyliminophenyl*-4-*ethoxydihydronaphthatriazine*,

$$OEt\cdot C_{10}H_5<\begin{matrix}NH\cdot C:NPh\\ NH\ \ NPh\end{matrix},$$

which crystallises from alcohol in colourless, lustrous needles and melts at 207°.

The *triazine*, $OEt\cdot C_{10}H_5<\begin{matrix}N\cdot C:NPh\\ N\cdot N\cdot C_{10}H_6\cdot OEt\end{matrix}$, prepared from the azo-compound, (4) $OEt\cdot C_{10}H_5(NH_2)\cdot N_2\cdot C_{10}H_6\cdot OEt$ (1 : 4), obtained from 1-amino-4-ethoxynaphthalene, crystallises in violet needles and melts at 275°; the salts are bright red.

Phenylethoxyketonaphthatriazine, $C_6H_4<\begin{matrix}C:N\cdot CO\\ C(OEt):CH\cdot C:N\cdot NPh\end{matrix}$, prepared by the action of carbonyl chloride on benzeneazoaminoethoxynaphthalene in benzene solution, crystallises from alcohol in yellow needles and melts at 236°.

Diazoamino-p-*anisole*, $OMe\cdot C_6H_4\cdot N_2\cdot NH\cdot C_6H_4\cdot OMe$, prepared from *p*-anisidine, crystallises from a mixture of ether and light petroleum in yellowish-brown prisms and melts at 101·5°; on attempting to convert it into *o*-aminoazoanisole, it gives rise to the *azophenine*, $C_6H_2(NH\cdot C_6H_4\cdot OMe)_2(:N\cdot C_6H_4\cdot OMe)_2$, derived from *p*-anisidine, which crystallises from a mixture of benzene and alcohol in red needles and melts at 242°.

Diazoamino-*p*-phenetole separates from a mixture of ether and light

petroleum in yellowish-brown crystals and melts at 119° (compare Henriques, Abstr., 1893, i, 39). W. A. D.

New Syntheses of Diazoamino-derivatives. IV. OTTO DIMROTH (*Ber.*, 1905, 38, 670—688).—*Phenylmethyltriazen* (diazobenzene-methylamine), N_3HMePh (Abstr., 1903, i, 450), prepared by adding phenylazoimide dissolved in ether to an ethereal solution of magnesium methyl iodide, and mixing at 0° the product with an aqueous solution of ammonium chloride containing ammonia, crystallises in long prisms, melts at 37—37·5°, and begins to decompose at 90°; it can, however, be distilled in a vacuum or by means of steam, and boils at 120° under 20 mm. pressure. The *silver* derivative, $N_3AgMePh$, crystallises from benzene on adding light petroleum and is rapidly decomposed by acids, nitrogen being evolved; the *cuprous* derivative forms large, orange prisms and begins to decompose at 180°. The following facts show that phenylmethyltriazen is capable of existing in the two isodynamic forms, $NHPh \cdot N_2Me$ and $NPh:N \cdot NHMe$, between which it is impossible to discriminate. With acids at 0°, decomposition occurs exclusively in the direction of the equation $NMe:N \cdot NHPh + 2HCl = MeCl + N_2 + NH_2Ph,HCl$, the theoretical quantity of aniline being formed. That this result does not occur in the following manner, (1) $NHMe \cdot N_2Ph + 2HCl = NH_2Me,HCl + N_2PhCl$; (2) $N_2PhCl + NH_2Me,HCl = NH_2Ph,HCl + MeCl + N_2$, is shown by the fact that a solution of benzenediazonium chloride is absolutely unaffected by methylamine hydrochloride at 0°. Phenylmethyltriazen is, moreover, decomposed by anhydrous hydrogen chloride in benzene solution, giving aniline only; it is also readily decomposed by acetic acid and by aqueous carbon dioxide. With phenylcarbimide, s.-*phenylmethylcarbamidoazobenzene*,

$$NHPh \cdot CO \cdot NMe \cdot N_2Ph,$$

is obtained; it crystallises from alcohol in lustrous, pale yellow needles, melts at 104°, and is quantitatively resolved by hydrogen chloride in benzene solution into *s.*-phenylmethylcarbamide and benzenediazonium chloride. *Acetylphenylmethyltriazen*,

$$NMeAc \cdot N_2Ph,$$

prepared by the action of acetic anhydride on phenylmethyltriazen dissolved in pyridine at 0°, separates from light petroleum in colourless, lanceolate crystals and melts at 35°. Attempts to methylate phenylmethyltriazen have as yet not been successful. Benzenediazonium chloride in alcohol at 0° converts it into *bisdiazobenzenemethylamide*, $NMe(N_2Ph)_2$.

Phenylmethyltriazen is reduced by zinc dust and ammonia principally to phenylhydrazine, but small quantities of aniline are obtained; reduction with sodium amalgam, however, gives rise to aniline and hydrazine.

Phenylethyltriazen, N_3HEt_2Ph, prepared from phenylazoimide and magnesium ethyl iodide, separates from light petroleum in thick crystals and melts at 31°; the crystalline *silver* derivative, $C_8H_{10}N_3Ag$, melts at 115° and the analogous *cuprous* derivative melts at 141°. It is decomposed by acids in the same way as the corresponding methyl derivative. With phenylcarbimide, it gives s.-*ethylphenylcarbamidoazobenzene*, $NHPh \cdot CO \cdot NEt \cdot N:NPh$, which crystallises

from alcohol in silky needles, melts at 99°, and is decomposed by hydrogen chloride in ethereal solution, giving phenylethylcarbamide,

NHPh·CO·NHEt,

and benzenediazonium chloride. *Acetylphenylethyltriazen*,

$NEtAc·N_2Ph$,

crystallises from light petroleum and melts at 26°.

The same phenylbenzyltriazen, $N_3HPh·CH_2Ph$, is obtained either by acting on phenylazoimide with magnesium benzyl chloride or by treating benzylazoimide with magnesium phenyl bromide. Its formation therefore corresponds with the two isodynamic formulæ, $NHPh·N_2·CH_2Ph$ and $NPh\colon N·NH·CH_2Ph$. With hydrochloric acid at 0°, moreover, it gives solely aniline hydrochloride and benzyl chloride, corresponding with the first formula, but, as stated by Goldschmidt and Holm (Abstr., 1888, 685), it behaves with phenylcarbimide as if it had the second of the two formulæ.

Benzylmethyltriazen, $N_3HMe·CH_2Ph$, is the first diazoamino-compound prepared containing the nitrogens combined on both sides with alkyl groups; prepared by the action of magnesium methyl iodide on benzylazoimide, it is purified by distillation and subsequent conversion into its silver derivative, the latter being then decomposed by alkaline aqueous sodium sulphide. It forms a colourless liquid which does not solidify on strongly cooling, decomposes slightly when distilled at 110—130° under 20 mm. pressure, and is very readily decomposed by acids, even by aqueous carbon dioxide, giving off the whole of its nitrogen. The *silver* derivative, $C_8H_{10}N_3Ag$, crystallises from ether in colourless, prismatic needles and melts at 125°; the *cuprous* derivative, $C_8H_{10}N_3Cu$, is also crystalline and melts at 114°.

W. A. D.

Diastasic Coagulation of Starch. JULES WOLFF and AUGUSTE FERNBACH (*Compt. rend.*, 1905, **140**, 95—97. Compare Abstr., 1903, i, 679; 1904, i, 211, 228, 294, 374; this vol., i, 164).—Malt extract which has been heated to destroy the amylocoagulase is still capable of causing diastasic coagulation in starch paste, and this affords further evidence in favour of the theory already advanced by the authors, namely, that in the diastasic formation of amylocellulose the coagulation is started by the diastase and then proceeds spontaneously (Abstr., 1904, i, 374). The formation of amylocellulose is stopped altogether either by adding to the starch paste excess of malt extract or by keeping it at a temperature of 60°; in each case, complete saccharification (liquefaction) is produced. Experiments conducted on starch paste which had been strongly heated under pressure showed that the state of liquefaction favourable to coagulation is equally favourable to the diastasic formation of amylocellulose.

M. A. W.

Organic Chemistry.

Composition of Petroleum CHARLES F. MABERY. **I. Hydrocarbons in Ohio Trenton Limestone Petroleum.** CHARLES F. MABERY and O. H. PALM. **II. Hydrocarbons in Canadian Petroleum with High Boiling Points. III. Hydrocarbons in Santa Barbara Crude Oil. IV. Separation of Solid Paraffin Hydrocarbons from Petroleum without Distillation.** CHARLES F. MABERY and OTTO J. SIEPLEIN. **V. The Solid Paraffin Hydrocarbons that collect in Oil Wells in Pennsylvania. VI. Composition of Commercial Paraffin. VII. Composition of Commercial Vaseline, Cosmoline, and Similar Products** (*Amer. Chem. J.*, 1905, 33, 251—292).—I. It has been shown previously (Abstr., 1897, i, 449) that the distillate, boiling at 212—214°, from Ohio Trenton limestone petroleum consists of dodecane, $C_{12}H_{26}$. A study has now been made of the higher boiling portions of the oil, and a number of hydrocarbons have been isolated by filtering the various fractions at $-10°$ and purifying the filtrates by treatment with fuming sulphuric acid. The results show that Ohio petroleum consists mainly of hydrocarbons of the series C_nH_{2n+2}, C_nH_{2n}, C_nH_{2n-2}, and C_nH_{2n-4}, and resembles Pennsylvania petroleum in containing a large proportion of solid hydrocarbons.

The following hydrocarbons have been separated, and their sp. gr. and refractive indices determined :

Series.	Formula.	From fraction boiling at				Sp. gr. at 20°.	Refractive index.
C_nH_{2n} ...	$C_{12}H_{24}$	211—213°	under	atmospheric	pressure	0·7970	1·4350
,, ...	$C_{13}H_{26}$	223—225	,,	,,	,,	0·8055	1·4400
,, ...	$C_{14}H_{28}$	138—140	,,	30 mm.	,,	0·8129	1·4437
,, ...	$C_{15}H_{30}$	152—154	,,	,,	,,	0·8204	1·4480
,, ...	$C_{16}H_{32}$	164—168	,,	,,	,,	0·8254	1·4510
,, ...	$C_{17}H_{34}$	177—179	,,	,,	,,	0·8335	1·4545
C_nH_{2n-2}..	$C_{19}H_{36}$	198—202	,,	,,	,,	0·8471	1·4614
,, ..	$C_{21}H_{40}$	213—217	,,	,,	,,	0·8546	1·465
,, ..	$C_{22}H_{42}$	224—227	,,	,,	,,	0·8614	1·4690
,, ..	$C_{24}H_{46}$	237—240	,,	,,	,,	0·8639	1·4715
C_nH_{2n-4}..	$C_{23}H_{42}$	253—255	,,	,,	,,	0·8842	1·4797
,, ..	$C_{24}H_{44}$	263—265	,,	,,	,,	0·8864	1·4802
,, ..	$C_{25}H_{46}$	275—278	,,	,,	,,	0·8912	1·4810

II. The constituents of Canadian Corniferous limestone petroleum which distil below 196° have been shown (*loc. cit.*) to be members of the series C_nH_{2n+2}, whilst above this temperature members of the series C_nH_{2n} appear. By distilling the higher fractions the following hydrocarbons have been separated.

The hydrocarbon, $C_{12}H_{24}$, boils at 216°; its *chloro*-derivative, $C_{12}H_{23}Cl$, boils at 160° under 15 mm. pressure and has a sp. gr. 0·9145 at 20°. The hydrocarbon, $C_{13}H_{26}$, boils at 228—230° under 15 mm. pressure and has a sp. gr. 0·7979 at 20° and n_D 1·444; the *chloro*-derivative, $C_{13}H_{25}Cl$, boils at 165° under 15 mm. and has a sp. gr. 0·9221 and n_D 1·465. The hydrocarbon, $C_{14}H_{28}$, boils at

141—143° under 50 mm. pressure and has a sp. gr. 0·8099 at 20° and n_D 1·449; the *chloro*-derivative, $C_{14}H_{27}Cl$, boils at 180° under 15 mm. pressure and has a sp. gr. 0·9288 at 20° and n_D 1·471; the *dichloro*-derivative, $C_{14}H_{26}Cl_2$, boils at 197—200° under 15 mm. and has a sp. gr. 1·0066 at 20° and n_D 1·489. The hydrocarbon, $C_{15}H_{30}$, boils at 159—160° under 60 mm. pressure and has a sp. gr. 0·8192 at 20° and n_D 1·452; the *chloro*-derivative, $C_{15}H_{29}Cl$, boils at 190° under 15 mm. pressure and has a sp. gr. 0·9358 at 20° and n_D 1·455.

III. A sample of crude petroleum from Santa Barbara County, Cal., which was of particular interest owing to its heavy, viscous character, was examined with the following results.

The oil had a sp. gr. 0·9845 at 20°, and the following composition: S, 0·84 per cent.; N, 1·25 per cent.; C, 86·32 per cent.; H, 11·70 per cent. The lower boiling fractions of the oil were found to consist of hydrocarbons of the series C_nH_{2n-2}, whilst the higher fractions contained hydrocarbons of the C_nH_{2n-4} and C_nH_{2n-8} series.

The following hydrocarbons were separated:

Hydrocarbon.	Boiling point under 60 mm. pressure.	Sp. gr. at 20°.	Refractive index.
$C_{13}H_{24}$	150—155°	0·8621	1·4681
$C_{16}H_{30}$	175—180	0·8808	1·470
$C_{17}H_{30}$	190—195	0·8919	1·4778
$C_{18}H_{32}$	210—215	0·8996	1·484
$C_{24}H_{44}$	250—255	0·9299	—
$C_{27}H_{46}$	310—315	0·9451	1·5146
$C_{29}H_{50}$	340—345	0·9778	—

IV. In order to demonstrate that the solid paraffin hydrocarbons are actually contained in crude petroleum and are not formed by decomposition, a sample of Pennsylvania petroleum was left in a draught of air until the residue ceased to lose weight or change in sp. gr. On cooling the product with ice, it solidified completely. When distilled, 28 per cent. collected below 300°, 6 per cent. below 360°, leaving a residue of 66 per cent. boiling above 360°. The amount of solid hydrocarbons in the residue was estimated by dissolving it in *iso*amyl alcohol and adding alcohol; the precipitate was collected and extracted with benzene. On evaporating the benzene solution, a greenish-black solid was obtained amounting to 39·6 per cent. of the heavy residue, or 14 per cent. of the original oil before evaporation. By repeated purification, a white substance was obtained which melted at 61°, had a sp. gr. 0·7966 at 70°, and the composition of a paraffin hydrocarbon.

V. The semi-solid product that collects in large quantities in certain oil wells in Pennsylvania has been investigated. The sample examined was a thick paste with sp. gr. 0·8345 at 60°. By fractional distillation and cooling the fraction with a mixture of ice and salt, the following solid hydrocarbons were isolated:

Hydrocarbon.	Formula.	Melting point.	Sp. gr.
Tetracosane	$C_{24}H_{50}$	50—51°	0·7900 at 60°
Hentriacontane ...	$C_{31}H_{64}$	66	0·7997 at 70
Dotriacontane	$C_{32}H_{66}$	67—68	0·8005 at 75
Tetratriacontane ...	$C_{34}H_{70}$	71—72	0·8009 at 80
Pentatriacontane ...	$C_{3}\ H_{72}$	76	0·8052 at 80

VI. A sample of commercial paraffin was distilled under 40 mm. pressure; the distillates collected between 250° and 350°, leaving a residue of only 2 per cent., whence it is evident that the solid hydrocarbons of commercial paraffin are members of the series C_nH_{2n+2}. The following hydrocarbons were isolated:

Hydrocarbon.	Formula.	Melting point.	Sp. gr.
Tri-icosane	$C_{23}H_{48}$	48°	0·7886 at 60°
Tetracosane	$C_{24}H_{50}$	50—51	—
Pentacosane	$C_{25}H_{52}$	53—54	0·7941 at 60
Hexacosane	$C_{26}H_{54}$	55—56	0·7968 at 60
Octacosane	$C_{28}H_{58}$	60	—
Nonacosane	$C_{29}H_{60}$	62—63	—

VII.—An examination of commercial vaseline (Ceroleum) has shown that this substance consists of heavy oils which form the high-boiling portion of Pennsylvania petroleum, hydrocarbons of the series C_nH_{2n}, C_nH_{2n-2}, and C_nH_{2n-4}, together with solid paraffin hydrocarbons.

E. G.

Action of Bromine on *iso*Butylene. S. A. Pogorželsky (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 1486—1505).—Linnemann and Zotta (this Journal, 1872, 476) only obtained *iso*butylene bromide on the interaction of bromine and *iso*butylene. The compounds isolated by the author as the products of this reaction, carried out under the conditions previously employed (this vol., i, 165) in studying the action of chlorine on *iso*butylene, are as follows: (1) a small quantity of *tert.*-butyl bromide, (2) *iso*butylene bromide, (3) *tribromo*iso*butane*,

$CH_2Br·CMeBr·CH_2Br$,

which is a colourless, heavy liquid, boils at 103° under 10 mm. and at 107° under 14 mm. pressure, and has the sp. gr. 2·2329 at 0°/0° and 2·1974 at 21°/0°. When treated with potassium acetate, it yields the *bromide-acetate*, $C_4H_6Br(C_2H_3O_2)$, which is a colourless liquid with a pleasant odour, boils at 193—194° under 766 mm. and at 96—97° under 18 mm. pressure, and has the sp. gr. 1·4278 at 0°/0° and 1·3997 at 22°/0°. Hydrolysis of this ester yields the corresponding *alcohol*, $OH·CH_2·CMe:CHBr$, as a colourless liquid which boils at 181—183° under 752 mm. pressure, has the sp. gr. 1·5611 at 0°/0° and 1·5406 at 18°/0°, and energetically decolorises bromine or potassium permanganate.

In the action of bromine on *iso*butylene, there are no unsaturated compounds formed, as is the case in the interaction of chlorine and *iso*butylene (*loc. cit.*).

When the products of the action of bromine on *iso*butylene are left in contact with water, *a*-*iso*butylene oxide is formed (compare Krassusky, Abstr., 1903, i, 8).

The action of bromine on *iso*crotonyl bromide gives the *tribromo*iso*butane*, $CMe_2Br·CHBr_2$, which boils at 96° under 14 mm. pressure and has the sp. gr. 2·2017 at 0°/0° and 2·1753 at 21°/0°. When treated with potassium acetate, this compound yields the unsaturated dibromide prepared by Norton and Williams (Abstr., 1887, 712).

T. H. P.

Mercury Nitroform and the Constitution of Salt Solutions. HEINRICH LEY (*Ber.*, 1905, **38**, 973—978).—Mercury nitroform dissolves in ether, benzene and its homologues, ethyl acetate, ethyl oxalate, chloroform, carbon tetrachloride, and lactic acid, giving colourless solutions; with alcohols, aliphatic ketones, acetic acid, dichloroacetic acid and nitriles, feebly yellow solutions are obtained, whilst the solutions in pyridine and water are strongly yellow. The solutions in pyridine and water have a considerable electrical conductivity, which is increased on dilution, especially in the case of water. It is assumed that the colourless solutions contain the compound $Hg[C(NO_2)_3]_2$, and the yellow solutions the coloured dissociating compound

$$Hg[O\cdot NO{:}C(NO_2)_2]_2.$$

Mercury nitroform combines with triethylamine to form the additive *compound* $C_2O_{12}N_6Hg,C_6H_{15}N$, which is so stable that it can be recrystallised from water. W. A. D.

Ferric Ethoxide. PAUL NICOLARDOT (*Compt. rend.*, 1905, **140**, 857—859).—Grimaux (Abstr., 1884, 573) has stated that when sodium ethoxide is added to a solution of anhydrous ferric chloride in absolute alcohol, pure sodium chloride is precipitated and ferric ethoxide remains in solution. The author finds that the precipitate is by no means pure sodium chloride, but that it contains very considerable quantities of iron. The alcoholic solution, moreover, always contains sodium. The conclusion is drawn that ferric ethoxide is not present in the alcoholic solution, and that there is no reason to assume the existence of such a substance. H. M. D.

Esters of Phosphorous Acid. ALEXANDER ARBUSOFF (*Ber.*, 1905, **38**, 1171—1173).—The esters of the type $P(OR)_3$ which have been hitherto described are really mixtures of the three esters $P(OR)_3$, $P(OR)_2\cdot OH$ and $PO(OR)_3$. The following substances were obtained pure by a lengthy fractional distillation, under diminished pressure, of the crude products:

Substance.	B. p. under 760 mm.	B. p. under 8—10 mm.	Sp. gr. at 0°.
$P(OMe)_3$	111—112°	—	1·0790
$P(OEt)_3$	155—156	49°	0·9777
$P(OPr^\alpha)_3$	206—207	83	0·9705
$P(OPr^\beta)_3$	—	60—61	0·9361
$P(OMe)_2\cdot OH$	—	56·5	1·2184
$P(OEt)_2\cdot OH$	187—188	72	1·0912
$P(OPr^\alpha)_2\cdot OH$	—	91	1·0366
$P(OPr^\beta)_2\cdot OH$	—	74—75	1·0159
$PO(OMe)_3$	192—193	72—73	1·2148
$PO(OEt)_3$	215—216	98—98·5	1·0897
$PO(OPr^\alpha)_3$	—	120·5—121·5	1·0282
$PO(OPr^\beta)_3$	—	95—96	1·0054
$PO(OC_4H_9)_3$*iso*	—	135—136	0·9698

The esters $P(OC_4H_9)_3$ and $P(OC_4H_9)_2\cdot OH$, derived from *iso*butyl alcohol, could not be separated; the mixture is a liquid boiling at 103—104° under 9 mm. pressure and having a sp. gr. 0·9275 at 0°/0°.

The esters of the type $P(OR)_3$ differ from those having the formulæ $P(OR)_2\cdot OH$ and $PO(OR)_3$ by forming definite compounds with the

cuprous haloids. The following table gives the properties of a series of these compounds:

Substance.	CuCl-compound. M. p.	CuBr-compound. M. p.	CuI-compound. M. p.
$P(OMe)_3,CuX$	190—192°	180—182°	175—177°
$2P(OMe)_3,CuX$ ...	—	—	69—70
$P(OEt)_3,CuX$	Liquid	27—28	109—110
$P(OPr^{\alpha})_3,CuX$ ...	Liquid	Liquid	64—65
$P(OPr^{\beta})_3,CuX$ ...	112—114	149—150	184—185
$P(OC_4H_9)_3,CuX$ ...	Liquid	Liquid	—
$P(OPh)_3,CuX$	95—96	90·5—91·5	—
$2P(OPh)_3,CuX$ ...	—	73—77	73—75

W. A. D.

Nomenclature of Compounds of Variable Constitution. Arthur Hantzsch (*Ber.*, 1905, **38**, 998—1004).—The author points out the necessity of having a simple and definite nomenclature for compounds which undergo intramolecular changes, and more particularly for acids and pseudo-acids, bases and pseudo-bases.

Examples are quoted to indicate the unsatisfactory nature of the present nomenclature. The author suggests the adoption of the following in the case of pseudo-acids and the isomeric true acids:

(1) If the name at present in use refers to the pseudo-acid, the prefix *aci-* attached to this name will designate the true acid.

The enolic derivatives of aldehydes and ketones would, therefore, according to this system be termed *aci*-aldehydes and *aci*-ketones, for example, *aci*-dibenzoylacetone, *aci*-diketopentamethylene. Ethyl β-hydroxycrotonate is termed ethyl *aci*-acetoacetate; hydroxymethylene compounds are termed *aci*-formyl compounds; salts of phenolphthalein are derivatives of *aci*-phenolphthalein; acid amides and imides give salts of *aci*-amides and *aci*-imides. Many other examples are mentioned.

In the event of this nomenclature being adopted, it would be necessary to alter the nomenclature of the diacipiperazines to diketopiperazines or piperazones.

(2) If the name at present in use refers to the true acid, the prefix *pseudo-* attached to this name will designate the pseudo-acid. Examples of the application of this nomenclature are quoted. Colourless violuric acid is *pseudo*-violuric acid. Cyanuric acid and uric acid are *pseudo*-cyanuric acid and *pseudo*-uric acid respectively on the assumption that they do not possess hydroxyl groups.

It is accordingly necessary to distinguish sharply between *pseudo*- and *iso*-compounds. A. McK.

Preparation of Acetyl Hydrogen Peroxide. Parke, Davis & Co. (D.R.-P. 156998).—When benzoyl acetyl peroxide is dissolved in water, hydrolysis takes place according to the equation $2OBz{\cdot}OAc + H_2O = O_2Bz_2 + HOAc + OAc{\cdot}OH$. The benzoyl peroxide is insoluble, and the solution of acetyl hydrogen peroxide and acetic acid may be employed directly for antiseptic purposes. C. H. D.

Rôle of Sulphuric Acid when Acetylating with Acetic Anhydride. OTTO STILLICH (*Ber.*, 1905, **38**, 1241—1246).—By the interaction of concentrated sulphuric acid and acetic anhydride, acetyl sulphuric acid is primarily formed at low temperatures; at higher temperatures, it rapidly changes to sulphoacetic acid. 3-*p*-Nitrophenyl-2-methyl-6-nitrodihydroquinazoline forms a sulphoacetate, decomposing at 268°, and an acetylsulphate decomposing at 213° (compare Abstr., 1903, i, 864).

The *ethyl sulphate* of nitrophenylmethylnitrodihydroquinazoline crystallises in faintly yellow prisms which sinter at 252° and decompose at 257—259°.

Barium sulphoacetate forms hydrogen sulphide, carbon dioxide, and a gas with a marked odour when heated at 350° in a metal bath. Sulphoacetic acid, obtained by decomposing the lead salt with hydrogen sulphide, melts at 84—86° and decomposes at 245°.

E. F. A.

Natural Heptadecoic Acid. DAVID HOLDE, LEO UBBELOHDE, and JULIUS MARCUSSON (*Ber.*, 1905, **38**, 1247—1258).—The heptadecoic acids, melting between 53° and 57°, described as occurring naturally in olive oil (Holde, Abstr., 1903, i, 140), pig fat (Kreis and Hafner, Abstr., 1903, i, 788), datura oil (Gérard, Abstr., 1890, 1395), and palm fat (Nördlinger, *Zeit. angew. Chem.*, 1892, 110), have been subjected to very careful fractionation with magnesium acetate in alcoholic solution and subsequent repeated crystallisation or distillation in a vacuum. They are shown in every case to be a mixture of palmitic, stearic, and other acids containing an even number of carbon atoms.

E. F. A.

Elaidin and Elaidic Acid. GAWALOWSKI (*Chem. Centr.*, 1905, i, 804; from *Pharm. Post*, **38**, 97—98).—On applying the elaidin test to a commercial oleic acid having a sp. gr. 0·934, melting point 30·7°, and solidification point 27°, and containing 4 per cent. of unsaponifiable matter, a mixture of a solid and a liquid elaidic acid was obtained at 17°.

The solid acid, amounting to 60 per cent., was nearly colourless and of tallowy odour, and had the sp. gr. 0·930, melting point 38°, and solidification point 23°, and contained 0·3 per cent. of unsaponifiable matter. The liquid acid, amounting to 30 per cent., was colourless and of faint fatty odour, and had the sp. gr. 0·936, melting point 16·5°, solidification point 14·9°, and contained 16·2 per cent. of unsaponifiable matter.

The author designates the solid *stereo-elaidic* and the liquid *oleo-elaidic* acid.

G. D. L.

***d*-Lactic Acid.** ÉMILE JUNGFLEISCH and MARCEL GODCHOT (*Compt. rend.*, 1905, **140**, 719—721. Compare Abstr., 1904, i, 645, 796).—The racemisation observed when quinine *d*-lactate is converted into the corresponding zinc salt (compare Abstr., 1904, i, 796) is due to the prolonged action of the barium hydroxide, and can be avoided by using cold saturated solutions of the salt and reagents in equiva-

lent quantities; crystalline zinc *d*-lactate thus prepared has the composition $Zn(C_3H_5O_3)_2,2H_2O$, and the rotatory power of its aqueous solutions increases with the dilution, solutions containing 5·0, 2·5, 1·25, and 0·512 grams of salt per 100 c.c. of solution have $[\alpha]_D$ $-6·0°$, $-8·0°$, $-11·1°$, and $-13·35°$ respectively at 15°. *d*-Lactic acid, obtained by Krafft and Dijes' method (Abstr., 1896, i, 84) or by a more simple process not yet described, crystallises in radiating clusters of prismatic needles melting at 25—26°, or 7° or 8° higher than the racemic acid; aqueous solutions of the pure acid are dextrorotatory, the value of $[\alpha]_D$ diminishing as the dilution increases, thus solutions containing 10·458, 5·022, 2·511, or 1·527 grams of $C_3H_6O_3$ per 100 c.c. have $[\alpha]_D$ $+3·82°$, $+3·33°$, $+2·67°$, or $+2·61°$ respectively at 15°. Wislicenus (compare Abstr., 1873, 57; 1874, 249; 1876, 561) also observed the variation of $[\alpha]_D$ with the concentration in the case of *d*-lactic acid and its zinc salt, but as he employed concentrated solutions which had been made for some time, it is probable that the changes in the rotation were due to the presence of *d*-lactyl-lactic acid which the author has shown to be formed when aqueous solutions of *d*-lactic acid are evaporated, and has $[\alpha]_D$ $-150°$; and not, as suggested by Wislicenus, to the presence of the *d*-lactide, which has $[\alpha]_D$ $-300°$.

Correction.—The values for $[\alpha]_D$ given previously (compare Abstr., 1904, i, 796) are not correct and require to be multiplied by the factor 4·332. M. A. W.

Ethoxycrotonic Acid and Ethylerythritic Acid. ROBERT LESPIEAU (*Compt. rend.*, 1905, **140**, 723—724).—*Ethyl γ-ethoxycrotonate*, OEt·CH$_2$·CH:CH·CO$_2$Et, obtained by distilling under reduced pressure ethyl β-hydroxy-γ-ethoxybutyrate (compare this vol., i, 255) with phosphoric oxide, boils at 201—203° under 760 mm. pressure, and on saponification yields *γ-ethoxycrotonic acid*,

OEt·CH$_2$·CH:CH·CO$_2$H,

a colourless, crystalline solid melting at 45°, boiling at 145—146° under 26 mm. pressure, and dissolving in ether, light petroleum, benzene, or alcohol. *α-Cyano-γ-ethoxypropylene* (γ-ethoxycrotononitrile), OEt·CH$_2$·CH:CH·CN, obtained by distilling β-hydroxy-γ-ethoxybutyronitrile with phosphoric oxide, is a colourless liquid which boils at 190—191° under 750 mm. pressure, solidifies in liquid methyl chloride, and readily combines with 1 mol. of hydrogen chloride. *γ-Ethylerythritic acid*, OEt·CH$_2$·[CH·OH]$_2$·CO$_2$H, obtained by oxidising barium γ-ethoxycrotonate with barium permanganate at 0°, crystallises from benzene and melts at 90—92°. M. A. W.

Condensation of Lævulic Acid with *iso*Butaldehyde. FRITZ MEINGAST (*Monatsh.*, 1905, **26**, 265—277).—When boiled with dilute sodium hydroxide in a reflux apparatus, *iso*butaldehyde and lævulic acid condense to form *iso*butylidenelævulic acid and octoglycol (Fossek, Abstr., 1884, 832). iso*Butylidenelævulic acid*,

CHPr^β:CH·CO·CH$_2$·CH$_2$·CO$_2$H,

is a yellow, odourless oil, which decomposes at about 230° under 10 mm. pressure, and with bromine in chloroform solution forms an

unstable *dibromide.* The *calcium*, $(C_9H_{13}O_3)_2Ca$, and the *silver*, $C_9H_{13}O_3Ag$, salts were analysed; the *ethyl* ester, formed from the acid by the action of alcohol and sulphuric acid, is a yellow liquid which boils at 150—155° under 16 mm. pressure. In aqueous sodium carbonate solution, *iso*butylidenelævulic acid is oxidised by permanganate in the cold to *iso*butyric and succinic acids. G. Y.

Acetyl-lactic [α-Acetoxypropionic] Acid. VICTOR AUGER (*Compt. rend.*, 1905, **140**, 938—939).—α-Acetoxypropionic acid, prepared by heating calcium lactate or lactic acid with acetyl chloride, or lactic acid with acetic anhydride, forms colourless, deliquescent crystals, melting at 39—40° and boiling at 167—170° under 78 mm. or 148—150° under 50 mm. pressure; its aqueous solution is stable, but as it is readily hydrolysed by metallic hydroxides, even in the cold, it is not possible to prepare its salts in a pure state. An attempt to prepare the acid by the hydrolysis of ethyl α-acetoxypropionate (compare Wislicenus, *Annalen*, 1863, **75**, 61) was unsuccessful, and the compound melting at 166°, obtained by Siegfried (compare Abstr., 1890, 128) from meat extract, was probably a polymeride or stereoisomeride of the acid described above. M. A. W.

Action of Allyl Iodide on Ethyl Succinate in presence of Zinc. γ-Diallylbutyrolactone. ALEXANDER KASANSKY (*J. pr. Chem.*, 1905, [ii], **71**, 249—257).—A mixture of 1 mol. of ethyl succinate and 2 mols. of allyl iodide was added to a mixture of finely granulated zinc and ether in a retort cooled by ice; after one month, water was added and the product extracted with ether and distilled. The fraction boiling at 244—250° contained ethyl γ-hydroxy-γ-diallybutyrate; that boiling at 250—270° contained γ-diallylbutyrolactone.

γ-Diallylbutyrolactone, $CH_2<\begin{matrix}C(C_3H_5)_2\\CH_2\cdot CO\end{matrix}>O$, is a viscid liquid which boils at 266—267°, and with aqueous alkali hydroxides, baryta, or calcium hydroxide yields the corresponding *salts* of γ-hydroxy-γ-diallylbutyric acid. With bromine in carbon tetrachloride solution, the lactone forms a *tetrabromide*, $C_4H_4O_2(C_3H_5Br_2)_2$, which crystallises in long, thin, white, rectangular plates, melts at 125—127°, and is highly refractive. With hydrogen iodide, under cooling, the lactone forms *γ-iodo-γ-diallylbutyric acid*, $C(C_3H_5)_2I\cdot CH_2\cdot CH_2\cdot CO_2H$, which is an oil, and is reduced by sodium amalgam in alcoholic sulphuric acid to *γ-diallylbutyric acid.* This is a liquid which boils at 264—267°; the *sodium* and *silver* salts are described. With bromine in carbon tetrachloride solution, γ-diallylbutyric acid forms a tribromolactone,

$$\begin{matrix}CH(C_3H_5Br_2)\cdot C_3H_5Br\\ CH_2\cdot CH_2 \text{———} CO\end{matrix}>O,$$

a reddish-brown, viscid liquid which fumes when anhydrous.

The oxidation of γ-diallylbutyrolactone by potassium permanganate in aqueous solution, under cooling, leads to the formation of a dibasic lactonic acid, which was isolated in the form of its *calcium* salt,

$$CO<\begin{matrix}CH_2\cdot CH_2 \;\; CH_2\cdot CO\cdot O\\ O\text{——}CH-CH-CO\cdot O\end{matrix}>Ca.$$

G. Y.

Influence of the Ethylenic Linkage in an [Optically] Active Molecule. JULES MINGUIN (*Compt. rend.*, 1905, **140**, 946—948).—The increased rotatory power of those derivatives of optically active substances which contain an ethylenic linkage has already been observed by Haller (Abstr., 1891, 1498; 1903, i, 503, 563, 628), Haller and Muller (Abstr., 1899, ii, 622), Eijkmann (Abstr., 1891, 919), Zelinsky (Abstr., 1902, i, 2, 597), Rupe (Abstr., 1903, i, 565), and by the author (Abstr., 1903, i, 428; 1904, i, 330; this vol., i, 130), and in the present paper it is shown that the esters of amyl alcohol or borneol have rotations which vary with the nature of the acid, being higher in the case of the unsaturated than in the case of the saturated acids. Amyl succinate, maleate, and fumarate gave α $+9°0'$, $+11°30'$, $+15°40'$ respectively in 20 cm. tubes, and amyl butyrate and crotonate gave α $+2°46'$ and $+3°30'$ in 10 cm. tubes (compare Guye, Abstr., 1895, i, 202, 318; Walden, Abstr., 1897, ii, 3). These esters were prepared by heating amyl alcohol and the corresponding acid, and the amyl alcohol regenerated from the esters was identical in optical activity with the original. Bornyl succinate and fumarate in alcoholic solution, 0·392 gram in 25 c.c. of alcohol, gave α $-1°22'$ and $-1°42'$ respectively in 20 cm. tubes, and bornyl butyrate and crotonate in alcoholic solution, 1·40 gram in 25 c.c. of alcohol, gave α $-4°30'$, $-4°44'$ respectively in 20 cm. tubes. M. A. W.

Action of Sulphuric Acid on Organic Acids. WILLIAM OECHSNER DE CONINCK and RAYNAUD (*Chem. Centr.*, 1905, i, 671; from *Rev. gen. Chim. pure appl.*, **8**, 61—62. Compare Abstr., 1903, i, 231, 457).—A higher acid containing a CH group is less stable towards hot sulphuric acid than one having a CH_2 group; a larger number of CH_2 groups or a longer chain also diminishing the stability. When the acids are gradually heated with an excess of glycerol, the gases evolved being led through concentrated sulphuric acid, sebacic acid gives a little carbon dioxide, glutaric and suberic acids are not decomposed, but the sulphuric acid becomes brownish-red and orange-red respectively. Ethyl-, methylethyl-, and *iso*propyl-malonic acids readily yield carbon dioxide; methylmalonic acid and its ethyl ester decompose more easily, alcohol and propionic acid being also formed from the latter substance. Anisic acid is not decomposed, but the sulphuric acid is coloured bright red; mucic and quinic acids are slowly decomposed, Bordeaux and reddish-pink colours respectively being produced. Alcohol is given off and a wine-red coloration of the acid produced by ethyl formate, ethyl acetate being equally stable. G. D. L.

Dimethyladipic and Trimethyladipic Acids. WILLIAM A. NOYES and HOWARD W. DOUGHTY (*Ber.*, 1905, **38**, 947—950. Compare Abstr., 1901, i, 631).—The acids previously described as di- and tri-methyl adipic acids are now shown to be respectively β-*iso*propyl- and α-methyl-β-*iso*propyl-glutaric acids (Blanc, Abstr., 1904, i, 647; Howles, Thorpe, and Udall, Trans., 1900, **77**, 942). A claim for priority in obtaining compounds with a trimethyl*cyclo*pentane ring from camphor is made (compare Perkin and Thorpe, Trans., 1904, **85**, 128). J. J. S.

Camphoric Acid. XIV. Derivatives of Trimethylparaconic Acid. WILLIAM A. NOYES (*Amer. Chem. J.*, 1905, **33**, 356—365. Compare Noyes and Patterson, Abstr., 1902, i, 741).—An improved method is described for the preparation of trimethylparaconic acid.

When diethyl trimethylitamalate is treated with phosphorus tribromide, *ethyl trimethylparaconate* is produced, which crystallises in needles, melts at 34—35°, and boils at 150—152° under 23 mm. pressure. *Trimethylparaconyl chloride*, $O\left\langle\begin{matrix}CO-CMe_2\\ CH_2\cdot CMe\cdot COCl\end{matrix}\right.$, is a crystalline substance which melts at 139—140° and is only slowly decomposed by water. The *amide* melts at 241—243° and is sparingly soluble in water, alcohol, ether, or benzene. When trimethylparaconic acid is heated with excess of barium hydroxide solution, *barium trimethylitamalate* is produced. If trimethylparaconyl chloride is heated with bromine in a sealed tube, the corresponding *bromide* is obtained, which melts at 125°, is sparingly soluble in ether, and when heated with alcohol at 230° yields ethyl trimethylparaconate together with the free acid.

An attempt was made to prepare ethyl hydroxytrimethyladipate lactone by the electrolysis of a mixture of potassium trimethylparaconate and potassium ethyl succinate, but the product consisted of a mixture of esters containing a large proportion of ethyl adipate together with a small quantity of *aa-dimethyl-β-methylenebutyrolactone*, $O\left\langle\begin{matrix}CO-CMe_2\\ CH_2\cdot C:CH_2\end{matrix}\right.$, which is an oily substance, volatile with steam, sparingly soluble in water, and instantly oxidised by potassium permanganate; the *silver* salt of the corresponding hydroxy-acid was prepared and analysed.

aaβ-Trimethylbutyrolactone, $O\left\langle\begin{matrix}CO-CMe_2\\ CH_2\cdot CHMe\end{matrix}\right.$, obtained by the reduction of ethyl trimethylparaconate, melts at 37° and boils at 211—212°; the *silver* salt of the corresponding hydroxy-acid was prepared and analysed.

By the action of trimethylparaconyl chloride on ethyl sodiomalonate, *ethyl ditrimethylparaconylmalonate*,

$$\left(CO\left\langle\begin{matrix}CMe_2-\\ O\cdot CH_2\end{matrix}\right\rangle CMe\cdot CO\right)_2C(CO_2Et)_2,$$

is obtained, which forms small, compact crystals and melts at 162—163°, together with *ethyl trimethylparaconylmalonate*,

$$CO\left\langle\begin{matrix}CMe_2-\\ O\cdot CH_2\end{matrix}\right\rangle CMe\cdot CO\cdot CH(CO_2Et)_2,$$

which boils at 250—255° under 60 mm. pressure and is converted by concentrated sodium hydroxide solution into a sparingly soluble *sodium* salt.

By the action of acetic anhydride on barium trimethylitamalate, *acetyltrimethylitamalic anhydride*, $CO\left\langle\begin{matrix}CMe_2\\ O\cdot CO\end{matrix}\right\rangle CMe\cdot CH_2\cdot OAc$, is produced, which boils at 185—195° under 20 mm. pressure; *trimethylparaconic anhydride*, $\left(CO\left\langle\begin{matrix}CMe_2-\\ O\cdot CH_2\end{matrix}\right\rangle CMe\cdot CO\right)_2O$, which is also pro-

duced in this reaction, forms small, granular crystals, melts at 154—155°, and can also be prepared by boiling trimethylparaconic acid with acetic anhydride. E. G.

Combination of Hydrogen Bromide with Itaconic Anhydride. LONGINUS ILSKY (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 116—118).—The action of hydrogen bromide on itaconic anhydride in chloroform solution and in complete absence of water yields: (1) bromopyrotartaric acid, melting at 134—135°, and (2) *bromopyrotartaric anhydride*, $CH_2Br\cdot CH<\begin{matrix}CO-O\\ CH_2\cdot CO\end{matrix}$, which separates from chloroform in crystals melting at 55—56° and has the normal molecular weight in freezing acetic acid. T. H. P.

Action of Methyl and Ethyl Chloro-oxalates on Cyanoacetic Esters. R. TRIMBACH (*Bull. Soc. chim.*, 1905, [iii], **33**, 372—375).—Ethyl cyano-oxalacetate, $CO_2Et\cdot CO\cdot CH(CN)\cdot CO_2Et$, prepared by the action of ethyl chloro-oxalate on the sodium derivative of ethyl cyanoacetate, melts at 96° (compare Bertini, Abstr., 1901, i, 776). *Methyl ethyl cyano-oxalacetate*, $CO_2Me\cdot CO\cdot CH(CN)\cdot CO_2Et$, similarly obtained from methyl cyanoacetate, melts at 102°. The *ethyl propyl ester*, $CO_2Pr^{\alpha}\cdot CO\cdot CH(CN)\cdot CO_2Et$, melts at 59° and the analogous *ethyl* iso*butyl* ester at 58°.

Methyl cyano-oxalacetate, $CO_2Me\cdot CO\cdot CH(CN)\cdot CO_2Me$, prepared by the action of methyl chloro-oxalate on methyl cyanoacetate, melts at 108°, the *methyl ethyl* ester, $CO_2Et\cdot CO\cdot CH(CN)\cdot CO_2Me$, at 85°, and the *methyl propyl* and *methyl* iso*butyl* esters at 73° and 65° respectively. T. A. H.

Ester-acids of Sulphur-substituted Carbonic Acids with Aliphatic Hydroxy-acids. B. HOLMBERG (*J. pr. Chem.*, 1905, [ii], **71**, 264—295. Compare Tröger and Volkmer, this vol., i, 15; Biilmann, *Dissert.*, Copenhagen, 1904).—*Diethyl xanthoformate*, $OEt\cdot CS\cdot S\cdot CO_2Et$, is formed by the action of potassium xanthate on ethyl chlorocarbonate, in aqueous solution, cooled by ice. On distilling the product under reduced pressure, a crystalline residue, probably diethyl xanthosulphoformate (Welde, this Journal, 1877, ii, 314), is obtained. Diethyl xanthoformate is a yellow oil, which boils at 133° under 18 mm., or at 149° under 50 mm. pressure, and has a sp. gr. 1·180 at 20°/4° and n_{Na} 1·527 at the laboratory temperature.

Ethyl xanthoacetic acid (*ethyl sulphothiocarboglycollic acid*),

$$OEt\cdot CS\cdot S\cdot CH_2\cdot CO_2H,$$

is obtained in the form of its *potassium* salt by the action of potassium ethyl xanthate on potassium chloroacetic acid in cooled aqueous solution. The acid crystallises in long, colourless prisms, melts at 57·5—58°, and has, with $\mu_{\infty} = 378$, a conductivity K 0·0649. The *sodium*, *calcium* (with $4H_2O$), *barium* (with $1\frac{1}{2}H_2O$), and *magnesium* (with $4H_2O$) salts are described. The methyl ester, $OEt\cdot CS\cdot S\cdot CH_2\cdot CO_2Me$ (Tröger and Volkmer, *loc. cit.*), boils at 154° under 24 mm. pressure and has a sp. gr. 1·218 at 20°/4°, and n_{Na}

1·535. *Diethyl xanthoacetate*, $OEt\cdot CS\cdot S\cdot CH_2\cdot CO_2Et$, is a yellow oil, which boils at 157° under 20 mm. pressure and has a sp. gr. 1·179 at 20°/4°, and n_{Na} 1·523. With potassium hydroxide in alcoholic solution, ethyl xanthoacetic acid yields potassium ethyl thiocarbonate, $OEt\cdot CO\cdot SK$, and potassium thioglycollate. When heated in aqueous solution on the water-bath, potassium ethyl xanthoacetic acid yields potassium thioglycollate, ethyl alcohol, carbon dioxide, and hydrogen sulphide; if the solution is cooled before the evolution of gas has ceased, the intermediate product, trithiocarbodiglycollic acid, is obtained. With aqueous ammonia at the ordinary temperature, ethyl xanthoacetic acid yields xanthamide and thioglycollic acid.

Methyl xanthoacetic acid, $OMe\cdot CS\cdot S\cdot CH_2\cdot CO_2H$, is obtained in the form of its *potassium* salt by the action of potassium methyl xanthate on potassium chloroacetate. The acid crystallises in colourless needles, melts at 38°, and is decomposed by water or potassium hydroxide in a similar manner to ethyl xanthoacetic acid. The *barium* salt (with $4H_2O$) crystallises in plates; the *ethyl* ester, $OMe\cdot CS\cdot S\cdot CH_2\cdot CO_2Et$, is a yellow oil, which boils at 158° under 32 mm. pressure and has a sp. gr. 1·225 at 20°/4° and n_{Na} 1·535.

Ethyl xantho-α-propionic acid (Tröger and Volkmer, *loc. cit.*), from potassium ethyl xanthate and potassium α-bromopropionate, crystallises in small, colourless, prismatic plates and melts at 49°; the *calcium* salt, $(OEt\cdot CS\cdot S\cdot CHMe\cdot CO_2)_2Ca,2H_2O$, crystallises in colourless, prismatic needles. Trithiocarbodilactic and thiolactic acids are formed by the action of hot water on ethyl xantho-α-propionic acid and its salts.

Ethyl xantho-β-propionic acid, $OEt\cdot CS\cdot S\cdot CH_2\cdot CH_2\cdot CO_2H$, obtained from β-iodopropionic acid and potassium xanthate, crystallises in colourless, prismatic needles, and, when acted on by ammonia, yields β-thiolactic acid and *β-dithiodilactic acid*, which melts at 156—157°. The *sodium* ($+3H_2O$) and the *calcium* ($+3H_2O$) salts are described.

The action of ethyl chlorocarbonate on potassium trithiocarbonate in aqueous solution leads to the formation of ethyl thiodicarbonate, $(OEt\cdot CO)_2S$ (Meyer, *Ber.*, 1869, **2**, 297), which boils at 119° under 24 mm. pressure, has a sp. gr. 1·123 at 20°/4°, and, when shaken with aqueous ammonia of sp. gr. 0·90, yields hydrogen sulphide and urethane.

Trithiocarbodiglycollic acid, $CS(S\cdot CH_2\cdot CO_2H)_2$, is formed by the action of potassium chloroacetate on potassium trithiocarbonate in aqueous solution, cooled by water, and addition of sulphuric acid to the product. It crystallises in thin, yellow leaflets or in rhombic plates and melts at 173·5—174°. The *potassium*, *sodium* ($+3H_2O$), *sodium hydrogen* ($+3H_2O$), *calcium* ($+H_2O$), and *barium* ($1\frac{1}{2}H_2O$) salts are described. The methyl ester crystallises in long, yellow, prismatic plates and melts at 32°; the *ethyl* ester crystallises in thin, glistening, yellow needles and melts at 47°. When boiled in neutral or alkaline aqueous solution, the acid yields thioglycollic acid and thiocarbamide; with alcoholic ammonia, the methyl ester yields *thioglycollamide*, $SH\cdot CH_2\cdot CO\cdot NH_2$, which crystallises in thin, white leaflets and melts at 149°.

Dithiocarbodiglycollic acid, $CO(S\cdot CH_2\cdot CO_2H)_2$, is formed by the

oxidation of the trithio-acid with potassium permanganate in aqueous potassium carbonate solution, cooled by ice, or by nitric acid of sp. gr. 1·40. It crystallises in thin leaflets, melts at 156°, and decomposes slowly in boiling water, more quickly in aqueous sodium carbonate solution, with formation of thioglycollic acid. The *sodium, sodium hydrogen* (with $3H_2O$), and *barium* (with $2\frac{1}{2}H_2O$) salts are described; the *ethyl* ester, obtained by oxidation of ethyl trithiocarbodiglycollate with nitric acid, crystallises in slender, white needles and melts at 49°.

Sulphothiocarbodiglycollic acid, $OH{\cdot}CO{\cdot}CH_2{\cdot}O{\cdot}CS{\cdot}S{\cdot}CH_2{\cdot}CO_2H$, was obtained by shaking carbon disulphide with an aqueous solution of potassium glycollate and treating the reaction product with chloroacetic acid. It crystallises in yellow plates and melts at 136°. The *sodium hydrogen* salt crystallises in thick, yellow plates; the *ethyl* ester forms stout, yellow needles and melts at 34—35°. When heated with water on the water-bath, the acid yields trithiocarbodiglycollic, glycollic, and thioglycollic acids, carbon dioxide, and hydrogen sulphide.

Trithiocarbodilactic acid, $CS(S{\cdot}CHMe{\cdot}CO_2H)_2$, formed by the action of α-bromopropionic acid on potassium trithiocarbonate in aqueous solution, is obtained in a yellow crystalline and a liquid modification, which gradually changes into the crystalline form.

Contrary to Biilmann's statement (*loc. cit.*), the successive action of hydrogen sulphide and carbon disulphide on potassium hydroxide in alcoholic solution leads to the formation of potassium trithiocarbonate and potassium xanthate. G. Y.

Presence and Formation of Formaldehyde in Various Combustions. AUGUSTE TRILLAT (*Bull. Soc. chim.*, 1905, [iii], **33**, 386—393).—Many of the results recorded in this paper have already appeared (Abstr., 1904, i, 713, and this vol., ii, 53). In the combustion of coal, peat, and various woods in cast-iron stoves, larger amounts of formaldehyde are produced than when these materials are burned in glass vessels. Soot contains varying quantities of trioxymethylene or paraformaldehyde. Formaldehyde is present in the gaseous products obtained by the incomplete combustion of oils, petroleum, and acetylene, and is formed during the combustion of sugar, juniper berries, incense, and other materials which have occasionally been employed in fumigation.

T. A. H.

Presence of Formaldehyde in the Atmosphere of Towns. AUGUSTE TRILLAT (*Bull. Soc. chim.*, 1905, [iii], **33**, 393—395. Compare preceding abstract; Henriet, Abstr., 1902, i, 714; 1903, i, 600; 1904, i, 289 and 649).—One hundred cubic metres of air examined on two different occasions on the roof of the Pasteur Institute yielded 24 and 17 mg. of formaldehyde respectively. The same quantities of air, collected half-way up the building, yielded respectively 31 and 25 mg. of the aldehyde, whilst from similar samples of air collected at Courbevoie 55 and 25 mg. respectively were obtained. Formaldehyde can be detected in air by exposing a slip of paper tinted

with rosaniline hydrochloride, which in presence of the aldehyde develops a blue colour. T. A. H.

Bromoacetal. Paul Freundler and Ledru (*Compt. rend.*, 1905, **140**, 794—796. Compare Abstr., 1892, 1424).—When acetal is treated with bromine in presence of calcium carbonate, the yield of bromoacetal is only about 50 per cent. of that required by theory. The chief by-product is bromoacetaldehyde, which is probably formed by hydrolysis of the bromoacetal. In order to improve the method of preparation, it is found advantageous to treat the product of bromination with a 2·5 per cent. solution of hydrobromic acid in alcohol. From 100 parts of acetal, 115 parts of bromoacetal can be thus obtained. Amongst the products of the reaction a small quantity of an oil boiling at 135·5—136·5° under 12—13 mm. pressure was found, which is probably a polymerised bromoacetaldehyde, for it dissociates at the ordinary temperature with the formation of the latter substance.

Bromoacetal is also formed by acting on paraldehyde with bromine at $-5°$ to $0°$ and treating the product with excess of absolute alcohol. Tetrabromobutaldehyde, $CH_2Br\cdot CHBr\cdot CBr_2\cdot COH$, is formed as a by-product in this reaction. *Bromomethyl acetal*, $CH_2Br\cdot CH(OMe)_2$, obtained in similar manner, boils at 53·5—54° under 21 mm. pressure. In alkaline solution, the bromine atom in the bromoacetals is readily replaced by the amino-, hydroxyl, or alkoxyl groups. When treated with finely divided magnesium at 110—115°, reaction takes place according to the equation $2CH_2Br\cdot CH(OEt)_2 + 2Mg = 2CH_2{:}CH\cdot OEt + MgBr_2 + Mg(OEt)_2$, and on further warming, the remaining bromoacetal reacts with the magnesium ethoxide according to the equation

$$2CH_2Br\cdot CH(OEt)_2 + Mg(OEt)_2 = 2OEt\cdot CH_2\cdot CH(OEt)_2 + MgBr_2.$$

H. M. D.

Action of Amyl Alcohol on Chloral Ethyl-alcoholate. Johannes Gadamer (*Arch. Pharm.*, 1905, **243**, 30).—When chloral ethyl-alcoholate, $CCl_3\cdot CH(OH)\cdot OEt$, is dissolved in amyl alcohol, the excess of the latter driven off at a gentle heat, and the syrupy residue crystallised from chloroform and light petroleum, chloral amyl-alcoholate,

$$CCl_3\cdot CH(OH)\cdot OC_5H_{11},$$

is obtained.

Attention is drawn to the analogy between this behaviour and that of certain substances denominated hydroxydihydro-bases (Decker, Abstr., 1893, i, 115); these must be supposed to react in a tautomeric aldehydic form (compare this vol., i, 368). C. F. B.

Action of Magnesium Amalgam on Acetone. François Couturier and Léon Meunier (*Compt. rend.*, 1905, **140**, 721—723. Compare Meunier, Abstr., 1902, i, 335).—Pure dry acetone (3 mols.) reacts energetically with magnesium amalgam (1 atom Mg) to form a compound of acetone and magnesium, probably $Mg{<}\begin{matrix}O\cdot CMe_2\\ |\\ O\cdot CMe_2\end{matrix}$, with 1 mol. of acetone of crystallisation, from which pinacone hydrate is obtained by the action of water. Attempts to prepare tetramethylethylene oxide, $O{<}\begin{matrix}CMe_2\\ |\\ CMe_2\end{matrix}$, by the dry distillation of the compound of acetone

and magnesium in a current of carbon dioxide at 250—300° were unsuccessful; the liquid distillate consisted of pinacoline with small quantities of acetone, *iso*propyl alcohol, and mesityl oxide. The author recommends this method of preparing pinacoline, as the yield (21 per cent. of the acetone) is far superior to that obtained by the ordinary process, starting from pinacone. M. A. W.

Mechanism of the Chlorination of Mixtures of Ketones and Water in presence of Marble. André Kling (*Bull. Soc. chim.*, 1905, [iii], **33**, 322—324).—When a slow current of chlorine is passed into a mixture of acetone and water in presence of marble (Fritsch, Abstr., 1893, i, 303; 1894, i, 490), the liquid becomes yellow; if the passage of chlorine is continued beyond this stage, an explosion may take place, and if the action of the gas is discontinued, the yellow colour disappears, slowly at the ordinary temperature and more rapidly on warming. By the application of Klimenko's method (Abstr., 1904, ii, 205), the author has found that the yellow liquid first produced is essentially a solution of hypochlorous acid and has confirmed this by showing that acetone is chlorinated by a solution of hypochlorous acid. T. A. H.

Transformation of Sugars showing Multirotation. Charles Tanret (*Bull. Soc. chim.*, 1905, [iii], **33**, 337—348. Compare Abstr., 1895, i, 321, 490; Lowry, Trans., 1899, **75**, 213; Armstrong, *ibid.*, 1903, **83**, 1305, and Behrend and Roth, Abstr., 1904, i, 716).—The author agrees that the β-forms of dextrose, lactose, and galactose, which he regarded as existing in aqueous solutions of these sugars which had acquired constant rotatory powers, are merely equilibrium mixtures of the two other forms (now denominated the α- and β-sugars) first described by him (*loc. cit.*), and he suggests that these equilibrium mixtures might conveniently be called the *s*-forms.

When α-dextrose is heated at 100°, it is converted into the β-form, and a similar change slowly occurs at the ordinary temperature: thus a specimen of α-dextrose had $[\alpha]_D$ $+22{\cdot}50°$ in 1895 and in 1904 this had fallen to $+19{\cdot}50°$. Similar changes take place with the α-forms of lactose and galactose. Small quantities of cold water transform the β-forms of dextrose and galactose slowly, but completely, into the α-forms: the reverse change takes place when the α-forms are heated in aqueous solution.

The relative proportions of the α- and β-forms of dextrose, galactose, and lactose which constitute the equilibrium mixtures (*s*-forms) of these three sugars are remarkably similar, being 0·368 : 0·632, 0·354 : 0·646, and 0·376 : 0·624 respectively. T. A. H.

Anilides of Rhamnose and Arabinose. Peter Hermann (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 119—120).—Both rhamnose and arabinose readily react with aniline in alcoholic solutions.

Rhamnose anilide, $C_6H_{12}O_4{:}NPh$, separates from alcohol in slender, white, acicular crystals which begin to decompose at about 110° and melt at 121—127°; in alcoholic solution, $[\alpha]_D$ has the value $-50{\cdot}4°$.

Arabinose anilide, $C_5H_{10}O_4{:}NPh$, separates from alcohol in slender, lemon-yellow crystals which begin to decompose at about 98° and melt at 103·5—106°. T. H. P.

Reversion of Artificial Starches. EUGÈNE ROUX (*Compt. rend.*, 1905, **140**, 943—946. Compare this vol., i, 262).—Artificial starches formed from starch or amylocellulose form, on solution, a paste which suffers a similar reversion under the influence of water, acids, or alkalis to that which the paste from the natural product undergoes (compare Abstr., 1903, i, 679; 1904, i, 17, 227, 228, 294, 800), only the change is more rapid in the former than in the latter case. The product of the reversion in each case has the same properties as the original starch and only becomes soluble at the temperature at which the original starch was soluble; the reversion is therefore a return to the initial state (compare Maquenne, Abstr., 1904, i, 294). M. A. W.

Replacement of Hydrogen Atoms, attached to a Nitrogen Atom, by Methyl Groups, by means of Formaldehyde. WILHELM ESCHWEILER (*Ber.*, 1905, **38**, 880—882. Compare D.R.-P. 80520, 1893).—The action of formaldehyde on ammonia, or on primary or secondary bases, or their salts, at 120—160°, results in the replacement of *N*-hydrogen atoms by methyl groups. At low temperatures, anhydro-derivatives are produced. With primary bases and with ammonia, the reaction takes place in two and three stages respectively. Hexamethylenetetramine yields as end-product in this reaction trimethylamine. G. Y.

Preparation of Trimethylamine by Methylation of Ammonia by means of Formaldehyde. ALBERT KOEPPEN (*Ber.*, 1905, **38**, 882—884. Compare preceding abstract).—A yield of 70—80 grams of trimethylamine hydrochloride is obtained by heating 50 grams of ammonium chloride with 440 grams of 40 per cent. formaldehyde solution in an autoclave at 120°. The reaction is finished when the internal pressure has reached a maximum of 35—40 atmospheres. G. Y.

Compounds of Tervalent Cobalt with Ethylenediamine. LUDWIG GERB (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 43—79).—The author first discusses the ethylenediamine-cobalt compounds already described by Werner (Abstr., 1901, i, 510, 511, 512), Jörgensen, and others.

1 : 2-*Dibromodiethylenediaminecobalt bromide*, 1 : 2($CoEnBr_2$)Br [En = ethylenediamine], separates from water in aggregates of black plates which, on crushing, yield a dark violet powder. When heated with concentrated hydrobromic acid, it is converted into the corresponding green 1 : 6-compound.

The action of sodium nitrite on 1 : 6-dichlorodiethylenediaminecobalt chloride yields : (1) the *flaveodiethylenediamine chloride*,

$$[CoEn_2(NO_2)_2]Cl,$$

which crystallises in large, monoclinic plates; (2) the *roseoethylenediamine chloride*, $[CoEn_2(NO_2)_2]Cl$, which crystallises from dilute hydrochloric acid in thin plates; (3) $(CoEnNO_2)NO_2$, which forms pale yellow, cubical crystals, and (4) certain secondary products in very small quantities.

Chloronitritodiethylenediaminecobalt chloride, ($CoEn_2Cl\cdot ONO$)Cl, separates from dilute hydrochloric acid in pale red, shining needles.

Chloronitritodiethylenediaminecobalt nitrate, $(CoEn_2Cl\cdot ONO)NO_3$, is obtained as a pale red, crystalline precipitate.

Chloronitritodiethylenediaminecobalt sulphate, $(CoEn_2Cl\cdot NO_2)HSO_4$, forms a red, amorphous precipitate.

Chloronitritodiethylenediaminecobalt nitrite, $(CoEn_2Cl\cdot NO_2)NO_2$, forms a yellow precipitate.

Chloronitritodiethylenediaminecobalt iodide, $(CoEn_2Cl\cdot NO_2)I$, forms a red, microcrystalline precipitate soluble in water.

Chloronitritodiethylenediaminecobalt bromide, $(CoEn_2Cl\cdot NO_2)Br$, forms a red, crystalline precipitate soluble in water.

Chloronitritodiethylenediaminecobalt thiocyanate, $(CoEn_2Cl\cdot NO_2)SCN$, is obtained as a red, crystalline precipitate soluble in water.

Nitritothiocyanodiethylenediaminecobalt chloride,

$$[CoEn_2(SCN)\cdot NO_2]Cl + 2H_2O,$$

forms deep yellow needles, or pale yellow leaflets, which do not effloresce in the air.

Thiocyanonitritodiethylenediaminecobalt iodide, $[CoEn_2(SCN)\cdot NO_2]I$, forms dark red, flat prisms soluble in water on prolonged boiling.

Thiocyanonitritodiethylenediaminecobalt nitrate,

$$[CoEn_2(SCN)\cdot NO_2]NO_3,$$

forms shining, badly developed plates soluble in water on prolonged boiling.

Thiocyanonitritodiethylenediaminecobalt bromide,

$$[CoEn_2(SCN)\cdot NO_2]Br,$$

forms small, drusy masses of a reddish-brown colour, readily soluble in water.

Thiocyanonitritodiethylenediaminecobalt thiocyanate,

$$[CoEn_2(SCN)\cdot NO_2]SCN,$$

forms large, yellowish-brown crystals soluble in water on long boiling. In acid solution, it gives, with potassium aurichloride, the *compound* $[CoEn_2(SCN)\cdot NO_2]AuCl_2$.

Nitritonitratodiethylenediaminecobalt nitrate, $[CoEn_2(NO_2)\cdot NO_3]NO_3$, forms a pale yellow, crystalline precipitate, and the corresponding *nitrite* slender, yellow crystals. T. H. P.

Characterisation of Lactones by means of Hydrazine. EDMOND E. BLAISE and A. LUTTRINGER (*Compt. rend.*, 1905, **140**, 790—792).—When lactones are heated on the water-bath with a slight excess of hydrazine hydrate until the water has been expelled, additive compounds, termed hydrazinolactones, are formed. These are very soluble in water and in alcohol, are nearly insoluble in ether, but can be easily crystallised from ethyl acetate solution. The chemical properties of the hydrazinolactones indicate that they are lactone additive compounds of the type $C{<}^{O}_{R}{>}C{<}^{OH}_{NH\cdot NH_2}$, and not hydrazides of the corresponding alcohol acids. Dilute sulphuric acid precipitates hydrazine sulphate from the aqueous solutions, and, when these are shaken with benzaldehyde, benzylideneazine is obtained. The crystalline substances slowly liberate hydrazine at 200°. The following derivatives were prepared. *Hydrazino-γ-methyl-*

butyrolactone, $\begin{matrix} CHMe\cdot O \\ | \\ CH_2\cdot CH_2 \end{matrix}\!\!>C(OH)\cdot NH\cdot NH_2$, melts at 61—62°; *hydrazino-αγ-dimethylbutyrolactone* melts at 115°; *hydrazino-βγ-dimethylbutyrolactone* melts at 96—97°; *hydrazino-α-methyl-γ-ethylbutyrolactone* melts at 124°, and *hydrazino-α-methyl-γ-*n-*amylbutyrolactone* melts at 116°. The method is also applicable to δ-lactones, but it is advisable to treat the lactone two or three times with hydrazine hydrate. *Hydrazino-α-methyl-δ-*n-*butylvalerolactone* was prepared; it melts at 76°. H. M. D.

Cyanuric Acid Derivatives. ARTHUR HANTZSCH and HUGO BAUER (*Ber.*, 1905, **38**, 1005—1013; compare this vol., i, 317).—The cyanilic acid described by Liebig is identical with cyanuric acid.

Isomeric esters of cyanuric acid are described. Methyl cyanurate, $C_3N_3(OMe)_3$, is prepared pure from cyanuric bromide and sodium methoxide; when cyanogen bromide is used instead of cyanuric bromide, mixtures of oily by-products are produced. Methyl cyanurate is readily hydrolysed by mineral acids at 100°. *Trimethyl* $\frac{1}{3}$-*ψ-cyanurate*, $N\!\!<\!\!\begin{matrix} CO\text{—}NMe \\ C(OMe)\cdot N \end{matrix}\!\!>\!\!C\cdot OMe$, is formed in small yield by careful alkylation with methyl iodide of silver cyanate at −5°, polymerisation occurring between 2 mols. of the true methyl cyanate and 1 mol. of the methyl ψ-cyanate. It melts at 105° and is distinguished from the other methyl cyanurates described in being volatile with steam and in subliming without undergoing decomposition. When heated in a sealed tube with hydrochloric acid, it is hydrolysed with the formation of *N*-monomethyl cyanurate, melting at 282° (Fischer gives 284—286° uncorr.) and forming a characteristic copper salt.

Trimethyl $\frac{2}{3}$-*ψ-cyanurate*, $N\!\!<\!\!\begin{matrix} CO\text{——}NMe \\ C(OMe)\cdot NMe \end{matrix}\!\!>\!\!CO$, is the main product of the action of trisilver cyanurate on methyl iodide at −10°, whilst trimethyl ψ-cyanurate is produced at higher temperatures. Trimethyl $\frac{2}{3}$-ψ-cyanurate melts at 118° and, when heated at 180°, is converted into trimethyl ψ-cyanurate, melting at 170°. When heated at 100° with concentrated hydrochloric acid, it undergoes hydrolysis to *N*-dimethyl cyanurate melting at 222°. Trimethyl ψ-cyanurate was also prepared.

Tribenzyl ψ-cyanurate, prepared from benzyl iodide and silver cyanate, melts at 165°; its *hydrochloride* melts and decomposes at 128°.

Ethyl tricyanotricarboxylate, $C_3N_3(CO_2Et)_3$, is trimolecular according to a determination of its molecular weight in chloroform. The free acid could not, however, be obtained from it owing to the ease with which decomposition occurs during hydrolysis.

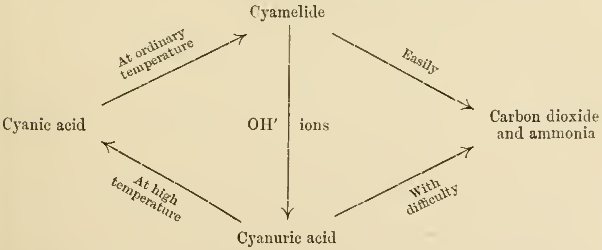
[With FRIEDRICH HOFMANN.]—*Tricyanocarbamide* (*cyanuric acid ureide*), $C_3N_3(NH\cdot CO\cdot NH_2)_3$, prepared by heating carbamide first at 130° and then gradually allowing the temperature to rise to about 200°, is freed from the cyanuric acid formed by removing the latter with water; it is an amorphous powder, and sublimes with decomposition at an elevated temperature. It differs from cyamelide in being soluble without decomposition in much boiling water. It

exhibits both acid and basic properties and is soluble in dilute alkalis. Its *trisodium* salt, $C_6H_6O_3N_9Na_3,5H_2O$, crystallises in tiny needles. The acid character of tricyanocarbamide is more marked than its basic character, since the substance separates unchanged from its solutions in dilute mineral acids.

Tricyanocarbamide is also formed by the following methods: by heating a mixture of cyanogen bromide and carbamide for 3 hours at 150° or in a sealed tube; by heating a mixture of cyanuric acid and carbamide at 180—190°, and by heating biuret. A. McK.

Cyanuric Acid Derivatives. OTTO DIELS (*Ber.*, 1905, 38, 1186—1188).—A criticism of certain statements made by Hantzsch and Bauer (preceding abstract). A. McK.

Cyamelide. ARTHUR HANTZSCH (*Ber.*, 1905, 38, 1013—1021).—Cyamelide is not produced together with cyanuric acid when carbamide is heated; tricyanocarbamide, which resembles cyamelide superficially, is, however, formed (compare preceding abstracts). The molecular weight of cyamelide, owing to the insolubility of the compound in the ordinary solvents, has not been determined directly. By indirect methods, it is shown that cyamelide is isomeric with cyanuric acid. Its formation from cyanic acid is a trimolecular reaction. Cyamelide is more readily decomposed than is cyanuric acid; by the action of sulphuric acid on the two isomerides, carbon dioxide and ammonia are formed at a lower temperature from cyamelide than from cyanuric acid. Cyamelide is more labile than cyanuric acid; it is accordingly the main product of the polymerisation of cyanic acid. That in many reactions cyamelide appears to be more stable than cyanuric acid is due to the latter being a *pseudo*-acid, which is convertible into the more reactive true acid. The relationships between cyanic acid, cyamelide, and cyanuric acid are expressed as follows:



Cyamelide is not a stereoisomeride of cyanuric acid or of *pseudo*-cyanuric acid. It cannot be regarded as a tricyanogen derivative; it cannot contain the group $\cdot N\colon C(OH)$ or the group $\cdot NH\cdot CO$, since it is neither a true acid nor a *pseudo*-acid.

Cyamelide is a polymeric form of ψ-cyanic acid, and is represented by the formula $NH\colon C\Big<\begin{matrix} O\cdot C(\colon NH) \\ O\cdot C(\colon NH) \end{matrix}\Big>O$.

[With Friedrich Hofmann and M. Lehmann.]—Oxalic acid and potassium cyanate were mixed at the ordinary temperature until the product, which was at first semi-liquid, solidified and until the odour of cyanic acid was no longer evident. On the addition of water, cyamelide was obtained as a white mass. Cyamelide is slightly soluble in water and in concentrated sulphuric acid. It is not acted on by phosphorus haloids, acetyl chloride, acetic anhydride, chlorine, or bromine. By the action of a 20 per cent. aqueous solution of sodium hydroxide, it is converted into trisodium cyanurate.

Monomercuric cyamelide, $(C_3O_3N_3)_2H_4Hg,3H_2O$, prepared by the action of freshly-prepared cyamelide on freshly-precipitated mercuric oxide in aqueous suspension, is insoluble in indifferent media and in ammonia, pyridine, dilute acids, and dilute alkali hydroxides. By the action of hydrogen sulphide or of alkali sulphides, mercuric sulphide is formed together with cyamelide. When heated at 180°, it is decomposed according to the equation: $3(C_3H_2O_3N_3)_2Hg,3H_2O = 3H_2O + (C_3O_3N_3)_2Hg_3 + 12HCON$. A. McK.

Transformations of Amides of α-Haloid Acids under the Action of Bromine and Alkali Hydroxide. Nic. M. Kijner (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 103—105).—The treatment of α-bromo*iso*butyric acid with bromine and potassium hydroxide, followed by distillation, yields: (1) β-dibromopropane and (2) a strongly alkaline liquid, which, when acidified with hydrochloric acid and distilled, gives 54 per cent. of the theoretical quantity of acetone. T. H. P.

Action of Hypochlorites on Carbamide: New Synthesis of Hydrazine. Petr J. Schestakoff (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 1—7).—The action of sodium hypochlorite on carbamide in alkaline solution proceeds in the following five stages:

1. $NH_2\cdot CO\cdot NH_2 + NaOCl = NH_2\cdot C(ONa)\colon NCl + H_2O$.
2. $NH_2\cdot C(ONa)\colon NCl = NH_2\cdot N\colon CCl\cdot ONa$.
3. $NH_2\cdot N\colon CCl\cdot ONa + NaOH = NH_2\cdot NH\cdot CO_2Na + NaCl$.
4. $NH_2\cdot NH\cdot CO_2Na + H_2O = NH_2\cdot NH_2 + NaHCO_3$.
5. $NH_2\cdot NH_2 + 2NaOCl = N_2 + 2H_2O + 2NaCl$.

The last phase only occurs when excess of the hypochlorite is used and it is more probable that it is not the hydrazine which undergoes decomposition but the sodium hydrazinecarboxylate. T. H. P.

Carbamide Derivatives of Natural (*l*) Leucine. Louis Hugounenq and Albert Morel (*Compt. rend.*, 1905, **140**, 859—861. Compare this vol., i, 178).—When one molecule of the ethyl ester of α-carbimino*iso*hexoic acid, $CO\colon N\cdot CH\cdot(CH_2Pr^{\beta})\cdot CO_2Et$, reacts with one molecule of ammonia in aqueous solution, the ethyl ester of *iso*butylhydantoic acid is obtained. When this is saponified and the solution acidified with mineral acid, the free acid,

$$NH_2\cdot CO\cdot NH\cdot CH\cdot(CH_2Pr^{\beta})\cdot CO_2H,$$

separates. It melts at 200° and is identical with the substance obtained by the action of leucine on carbamide (*loc. cit.*).

When aniline is substituted for ammonia in the above reaction, the acid, $NHPh\cdot CO\cdot NH\cdot CH(CH_2Pr^{\beta})\cdot CO_2H$, is obtained. It crystallises

in slender needles, melts at 115°, and is only slightly soluble in cold water, but more readily soluble in hot water, in alcohol, or ether.

When ethyl *a*-carbimino*iso*hexoate (1 mol.) is gradually added to a cooled alkaline solution of *l*-leucine (1 mol.), it slowly passes into solution; after saponification and addition of a mineral acid, the symmetrical *a*-*iso*hexoic acid derivative of carbamide,

$$OC[NH\cdot CH\cdot (CH_2Pr_\beta)\cdot CO_2H]_2,$$

is precipitated. It crystallises with difficulty, dissolves only slightly in cold water, more readily in hot. It is soluble in ether and benzene and very soluble in alcohol. Its alkali and copper salts are soluble, the lead and silver salts insoluble. H. M. D.

Oxidation of Pyrrole to Maleimide. GIUSEPPE PLANCHER and C. RAVENNA (*Atti R. Accad. Lincei*, 1905, [v], 14, i, 214—216).—The maleimide prepared by the oxidation of pyrrole (see Plancher and Cattadori, Abstr., 1904, i, 770) crystallises in the triclinic system [G. Boeris gives: $a:b:c = 1\cdot0686:1:0\cdot8648$; $\alpha = 90°15'$, $\beta = 105°7'$, $\gamma = 108°53'$]. It is not identical with the isomeric fumarimide obtained from ammonium malate, and when boiled with sodium hydroxide solution yields ammonia and maleic acid. With phenylhydrazine, it yields *maleamide-phenylhydrazide*, $NH_2\cdot CO\cdot CH{:}CH\cdot CO\cdot NH\cdot NHPh$, which separates from alcohol in pale yellow crystals melting at 147—148°; the *amide anilide*, $NH_2\cdot CO\cdot CH{:}CH\cdot CO\cdot NHPh$, is deposited from benzene in pale yellow crystals melting at 173—175°. T. H. P.

New General Methods of Hydrogenation and of Molecular Reactions based on the use of Finely Divided Metals. I. PAUL SABATIER and JEAN B. SENDERENS (*Ann. Chim. Phys.*, 1905, [viii], 4, 319—432).—The experimental results described in this paper have already been published (compare Abstr., 1900, i, 421, 469, 470, 471, 534; 1901, i, 195, 263, 459, 638; 1902, i, 333, 525, 581, 701; ii, 317, 605; 1903, i, 393, 453, 454, 686, 733; 1904, i, 156, 303, 305, 660; this vol., i, 254; compare also Brunel, Abstr., 1904, i, 158). For a detailed description of the method of employing this new process of hydrogenation, the original must be consulted; the activity of the metal, or catalyst, in this process like that of a living ferment, exhibits three distinct phases: the initial phase, usually of short duration, corresponds with the superficial modification of the metal due to the replacement of the atmosphere of hydrogen by one of the vaporised compound; the second or normal phase is usually of long duration, in the case of the hydrogenation of benzene to *cyclo*hexane the same quantity of nickel was used almost continuously for over a month; whilst the third phase corresponds with the decay in the activity of the metal due to a change in its surface, brought about by traces of the halogen elements, or of sulphur, or by a decomposition of carbonaceous or tarry matter, especially if the hydrogenation has been conducted at a high temperature.

Eijkman (compare *Chemisch Weekblad*, I. 7; *Chem. Centr.*, 1903, [ii], 989) has employed the method of hydrogenation described in this paper to convert hydrindene into di*cyclo*nonane boiling at 163°;

diphenylmethane into di*cyclo*hexylmethane boiling at 251°; diphenyl into phenyl*cyclo*hexane boiling at 238° under 770 mm. pressure and crystallising at 0°; *cyclo*pentadiene into pentamethylene boiling at 49°; and di*cyclo*pentadiene into tri*cyclo*decane boiling at 193°, melting at 77°, and having an odour of camphor. M. A. W.

Combination of Hydrocarbons or of Hydrogen Chloride with Compounds of Aluminium Chloride which act as Ferments. GABRIEL GUSTAVSON (*Compt. rend.*, 1905, **140**, 940—941. Compare Abstr., 1903, i, 470, 804).—When aluminium chloride is added to a mixture of benzene and *iso*propyl chloride at a low temperature, the *compound* $Al_2Cl_6,2C_6H_3Pr^{\beta}_3,HCl$ is obtained in the form of yellow crystals which are decomposed by water yielding *tri*iso*propylbenzene*, and melt and decompose at 50° forming tri*iso*propylbenzene, hydrogen chloride, and the compound $Al_2Cl_6,C_6H_3Pr^{\beta}_3$; this acts as a ferment, combining with benzene to form the compound $Al_2Cl_6,C_6H_3Pr^{\beta}_3,6C_6H_6$, which reacts with *iso*propyl chloride to form the yellow, crystalline substance described above. The *compound* $Al_2Cl_6,C_6H_3Et_3,HCl$, obtained by the action of hydrogen chloride on $Al_2Cl_6,C_6H_3Et_3$ and $C_6H_3Et_3$ at −10°, forms yellow crystals, and the *compound*

$$Al_2Cl_6,C_6H_3Et_3,C_6H_3Pr^{\beta}_3,HCl,$$

similarly prepared, is also yellow.

*Tri*iso*propylbenzene*, prepared as above, boils at 234—236° and the magnesium salt of its sulphonic derivative, $(C_6H_2Pr^{\beta}_3SO_3)_2Mg,7H_2O$, is very sparingly soluble, one part of the salt dissolving in 1414 parts of water at 19°. M. A. W.

Monochloro-derivatives of Methyl*cyclo*hexane. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1905, **140**, 840—843. Compare Abstr., 1903, i, 686).—When methyl*cyclo*hexane is treated with chlorine at the ordinary temperature together with other products, a mixture of monochloro-substitution products is obtained. To ascertain the nature of these, the authors have prepared the five possible chloromethyl*cyclo*hexanes by action of phosphorus pentachloride on the corresponding hydroxy-compounds.

Hexahydrobenzyl chloride, $C_6H_{11}\cdot CH_2Cl$, is a colourless liquid of sp. gr. 1·0038 at 0°/0°, which boils at 166° (corr.) under 760 mm. without sensible decomposition. 2-*Chloromethyl*cyclo*hexane* has a sp. gr. 1·001 at 0°/0° and boils at 156° with slight decomposition; 3-*chloromethyl*cyclo*hexane* has a sp. gr. 1·011 at 0°/0° and boils at 157° with slight decomposition; 4-*chloromethyl*cyclo*hexane* has a sp. gr. 0·992 at 0°/0° and boils at 158°, decomposing appreciably. 1-Chloromethyl*cyclo*hexane has a sp. gr. 0·996 at 0°/0° and boils at 148—151° with considerable decomposition. From these data, it is concluded that the product of chlorination of methyl*cyclo*hexane contains neither hexahydrobenzyl chloride nor 1-chloromethyl*cyclo*hexane.

In the further investigation of the nature of the product of chlorination, this was converted by Grignard's method into magnesium methyl*cyclo*hexyl chloride, which on prolonged oxidation in a current of pure dry oxygen and treatment with cold water gives the alcohols corresponding to the chloro-derivatives.

From the results so obtained, it is considered that the monochloro-derivatives formed by direct chlorination of methyl*cyclo*hexane consist of about 40 per cent. of 2-chloromethyl*cyclo*hexane and about 60 per cent. of the 3-derivative associated with a little 4-chloromethyl*cyclo*hexane. H. M. D.

Removal of Halogens from the Benzene Nucleus by the Action of Sodium and Ethyl Alcohol. A. Stepanoff (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 12—16).—In order to remove the halogen contained in the benzene nucleus of an aromatic compound, the author takes a definite weight of the latter and heats on a water-bath in a reflux apparatus with 20—40 c.c. of 98 per cent. alcohol, sodium being dropped in small pieces down the condenser tube until the total amount added is about 25 times that required by the equation:

$$RCl + EtOH + Na_2 = RH + NaCl + EtONa.$$

When the sodium is all dissolved, from 20 to 40 c.c. of water are added and the alcohol then distilled off. On cooling, the contents of the flask are strongly acidified by the addition of dilute nitric acid and the halogen determined by titration according to Volhard's method. When treated in this way, chlorobenzene, hexachlorobenzene, bromobenzene, *p*-chlorotoluene, and bromonaphthalene give up the whole of the halogen they contain. The method may hence be used as a means of estimating the halogen in these compounds. T. H. P.

Chemical Action caused by Light. VIII. Giacomo Ciamician and Paul Silber (*Ber.*, 1905, **38**, 1176—1184).—When a mixture of benzaldehyde and nitrobenzene is exposed to light for several months, the following substances are formed: benzoic acid, dibenzoylphenylhydroxylamine, NPhBz·OBz; benzoylphenylhydroxylamine, NPhBz·OH; dibenzoyl-*p*-aminophenol; *o*-benzoylaminophenol, benzanilide, azoxybenzene, and *o*-hydroxyazobenzene. The proportion of the last two substances is increased by increasing the time of exposure to light; they are formed at the expense of the benzoylphenylhydroxylamine and *o*-benzoylaminophenol. A theory of the mechanism of the interaction is given, based on Bamberger's experiments on the decomposition of nitrosobenzene (Abstr., 1900, i, 531, and 1902, i, 505). W. A. D.

Uses of Metallic Calcium. Ernst Beckmann [with Karl Beck and Hans Schlegel] (*Ber.*, 1905, **38**, 904—906).—Nitrobenzene is reduced by calcium in alcoholic solution, in presence of mercuric chloride or copper sulphate, to azoxybenzene, or in alcoholic hydrochloric acid solution to aniline. Benzenesulphonic chloride is reduced by calcium in alkaline solution to the sulphinic acid, but in acid solution to thiophenol; whilst oximes are reduced in either solution to amines.

When boiled with iodobenzene in absolute ethereal solution containing traces of iodine, calcium forms *calcium phenyl iodide*, which is obtained as a brown powder and is moderately soluble in ether. When treated with carbon dioxide and water, successively, it yields benzoic acid; with benzaldehyde and water, it forms benzhydrol.

Calcium and ethyl iodide do not react when boiled in benzene, but in ethereal solution an *additive* compound of ether and calcium ethyl iodide, $OEt_2,CaEtI$, is formed as an odourless, white substance which is stable on exposure to air, but decomposes at 40°, and when treated with water yields ethane.

Metallic oxides and sulphides may be reduced to the metals by calcium instead of aluminium, by Goldschmidt's method (Abstr., 1898, ii, 509). G. Y.

Amides, Nitriles, and Thioamides of Arylsulphonacetic Acids. JULIUS TRÖGER and WALDEMAR HILLE (*J. pr. Chem.*, 1905, [ii], 71, 201—235. Compare Otto, Abstr., 1885, 535).—Arylsulphonacetamides are formed by the action of chloroacetamide on sodium arylsulphonates in boiling alcohol solution or, when moistened with alcohol, in a sealed tube at 100°. Benzenesulphonacetamide, $SO_2Ph\cdot CH_2\cdot CO\cdot NH_2$, crystallises in glistening, white needles and melts at 156° (m. p. 153°, Otto, *loc. cit.*). p-*Toluenesulphonacetamide* crystallises in slender, white needles, melts at 166°, and dissolves easily in alcohol or ethyl acetate. *o-Toluenesulphonacetamide* crystallises in slender, white needles and melts at 144°.

To prepare *m*-toluenesulphinic acid by Gattermann's method, *m*-toluidine is diazotised in dilute solution, in presence of a large excess of acid; the treatment with sulphur dioxide must not be too prolonged, and the copper powder must be added before the appearance of the red precipitate (Abstr., 1904, i, 118). m-*Toluenesulphinic acid* is an unstable oil, which is only slightly soluble in cold ether; the *sodium* and *barium* salts were prepared. m-*Toluenesulphonacetamide* crystallises in slender, white needles and melts at 146°. 1:3-*Xylene*-4-*sulphonacetamide* crystallises in soft needles and melts at 149°. p-*Chlorobenzenesulphonacetamide* crystallises in long, glistening needles and melts at 169°. p-*Bromobenzenesulphonacetamide* crystallises in stout, white needles and melts at 166°. p-*Iodobenzenesulphonacetamide* forms small, white crystals and melts at 189°. *a-Naphthalenesulphonacetamide* forms a yellow, crystalline powder and melts at 162°. *β-Naphthalenesulphonacetamide* separates from alcohol as a white, crystalline powder and melts at 194°.

The action of bromine on benzenesulphonacetamide in glacial acetic acid solution leads to the formation of *benzenesulphonbromoacetobromoamide*, $SO_2Ph\cdot CH\cdot Br\cdot CO\cdot NH\cdot Br$, which crystallises in glistening, white leaflets, melts at 139°, dissolves readily in hot alcohol, and liberates iodine from potassium iodide in acid solution, and when acted on by 3 mols. of potassium hydroxide in 30 per cent. warm aqueous solution or by sodium ethoxide, yields phenyldibromomethylsulphone, $CHBr_2\cdot SO_2Ph$. Phenyltribromomethylsulphone, $CBr_3\cdot SO_2Ph$, is formed by the action of bromine and aqueous sodium hydroxide on benzenesulphonacetamide or on phenyldibromomethylsulphone; it crystallises in glistening, white needles and melts at 145°. The action of chlorine on benzenesulphonacetamide in glacial acetic acid solution leads to the formation of *benzenesulphondichloroacetochloroamide*, $SO_2Ph\cdot CCl_2\cdot CO\cdot NHCl$, which crystallises in thick, white, glistening needles, melts at 144°, and when treated with 30 per cent. potassium

hydroxide solution yields a *product*, which is probably phenyltrichloromethylsulphone. p-*Toluenesulphonacetobromoamide,* formed by the action of 1 mol. of bromine on *p*-toluenesulphonacetamide, crystallises in white needles and melts at 177°. With an excess of bromine, p-*toluenesulphonbromoacetobromoamide* is obtained, crystallising in prisms, melting at 138°, and when warmed with aqueous potassium hydroxide yielding *p*-tolyldibromomethylsulphone, which is also formed by the action of bromine and aqueous sodium hydroxide on *p*-toluenesulphonacetamide. p-*Toluenesulphonchloroacetochloroamide,* obtained by the action of chlorine on *p*-toluenesulphonacetamide, forms white crystals, melts at 124°, and when treated with aqueous sodium hydroxide yields an oily *product.* *β-Naphthalenesulphondibromoacetobromoamide* forms a white, crystalline powder, melts at 172—174°, and is converted by aqueous potassium hydroxide into *β-naphthyldibromomethylsulphone,* which melts at 108—112°; impure *β-naphthyltribromomethylsulphone,* melting at 150—160°, is obtained by the action of bromine and aqueous sodium hydroxide on *β*-naphthalenesulphonacetamide. The action of chlorine on *β*-naphthalenesulphonacetamide leads to the formation of an impure *tetrachloro*-derivative melting at 94°.

Arylsulphonacetonitriles are formed by the action of chloroacetonitrile on sodium arylsulphonates. *Benzenesulphonacetonitrile,* $SO_2Ph{\cdot}CH_2{\cdot}CN$, crystallises in glistening, white needles, melts at 114°, and is moderately soluble in alcohol, but only slightly so in water. When treated with alcohol and hydrogen chloride, in ethereal solution, it yields the *hydrochloride* of benzenesulphonacetiminoethyl ether,

$$SO_2Ph{\cdot}CH_2{\cdot}C(OEt){:}NH,HCl,$$

which forms small, white crystals. p-*Toluenesulphonacetonitrile* forms white, refractive crystals and melts at 145—146°. o-*Toluenesulphonacetonitrile* is obtained as an oil, which gradually solidifies to a crystalline mass. m-*Toluenesulphonacetonitrile* crystallises in needles and melts at 168°. 1 : 3-*Xylene-4-sulphonacetonitrile* crystallises in white needles and melts at 79—80°. *α-Naphthalenesulphonacetonitrile* crystallises in long needles and melts at 109°. *β-Naphthalenesulphonacetonitrile* forms small crystals and melts at 95°. *p*-Chlorobenzenesulphinic acid is prepared by Gattermann's method from *p*-chloroaniline; from *p*-chlorobenzenesulphonic chloride, by Otto and Schiller's method; and from sodium *p*-chlorobenzenethiosulphonate by the action of mineral acids or of aqueous potassium cyanide solution. p-*Chlorobenzenesulphonacetonitrile* forms glistening, white crystals and melts at 169°. p-*Bromobenzenesulphonacetonitrile* forms small, glistening crystals and melts at 194°. p-*Iodobenzenesulphonacetonitrile* is crystalline and melts at 213—214°. m-*Phenylenedisulphonacetonitrile,* $C_6H_4(SO_2{\cdot}CH_2{\cdot}CN)_2$, is crystalline and melts at 164°. 1 : 2 : 4-*Tolylenedisulphonacetonitrile* crystallises in small needles and melts at 179°. With sodium in absolute alcoholic solution, or with cold dilute aqueous sodium hydroxide, arylsulphonacetonitriles form *monosodium* and *disodium* derivatives, which are soluble in water and are decomposed by a current of carbon dioxide. When treated with reducing agents, arylsulphonacetonitriles remain unchanged, or are decomposed to sulphinic acids.

Arylsulphonthioacetamides are formed by the action of hydrogen sulphide on arylsulphonacetonitriles in presence of alcoholic ammonia

at the ordinary temperature. *Benzenesulphonthioacetamide*,

$$SO_2Ph\cdot CH_2\cdot CS\cdot NH_2,$$

forms yellow crystals, melts at 170°, and forms a *sodium* derivative, which is soluble in water and is decomposed by carbon dioxide. It is reduced by alcoholic hydrochloric acid and zinc dust to hydrogen sulphide and phenyl mercaptan, which is oxidised by the oxygen of the air to phenyl disulphide; by aluminium in alkaline solution to phenyl-mercaptan and ammonia. p-*Toluenesulphonthioacetamide* crystallises in long, yellow needles and melts at 179°. m-*Toluenesulphonthioacetamide* forms a white, crystalline powder and melts at 142°. 1 : 3-*Xylene-4-sulphonthioacetamide* forms small, yellow crystals and melts at 118°. *a-Naphthalenesulphonthioacetamide* forms small, yellow crystals and melts at 204°. *β-Naphthalenesulphonthioacetamide* forms small, yellow crystals and melts and decomposes at 170°. p-*Chlorobenzenesulphonthioacetamide* melts at 181°. p-*Bromobenzenesulphonthioacetamide* forms small, glistening, yellow crystals and melts at 207°. p-*Iodobenzenesulphonthioacetamide* forms a yellow, crystalline powder and melts at 203°. m-*Phenylenedisulphonthioacetamide*, $C_6H_4(SO_2\cdot CH_2\cdot CS\cdot NH_2)_2$, forms a grey powder and melts at 189°. G. Y.

Hydrides of Phenanthrene. PIERRE BRETEAU (*Compt. rend.*, 1905, **140**, 942—943. Compare Graebe, Abstr., 1873, 896; Bamberger and Lodter, Abstr., 1888, 292; Liebermann and Spiegel, Abstr., 1889, 719).—When phenanthrene is directly hydrogenated in the presence of reduced nickel at 200° by Sabatier and Senderens' method, a mixture of hexahydro- and octohydro-phenanthrene is obtained which can be separated by fractional distillation.

Hexahydrophenanthrene, $C_{14}H_{16}$, is a pale yellow liquid, boiling at 305—307° under 760 mm. or at 165—167° under 13 mm. pressure; it melts at −3°, has a sp. gr. 1·053 at 0° or 1·043 at 15°, and n_D 1·580 at 15°; is soluble in alcohol, acetic acid, ether, benzene, or chloroform; forms a *picrate* melting at 106° and two solid bromine *derivatives* melting at 150° and 142° respectively; it is readily oxidised by dilute nitric acid, potassium permanganate, or chromic acid, but does not yield phenanthraquinone. Octohydrophenanthrene, $C_{14}H_{18}$ (compare Graebe, Abstr., 1873, 896), is a colourless liquid boiling at 280—285° under 760 mm., or at 123—124° under 13 mm. pressure; it has a sp. gr. 1·006 at 0°, or 0·993 at 15°, n_D 1·537 at 15°; is slightly soluble in cold, more readily so in hot alcohol, very soluble in ether, benzene, or chloroform; it does not form a solid picrate, it yields unstable liquid bromine derivatives, and behaves towards oxidising agents in the same way as the hexahydro-compound.

M. A. W.

Separation of Primary and Secondary Amines. OSCAR HINSBERG and J. KESSLER (*Ber.*, 1905, **38**, 906—911. Compare Abstr., 1891, 49; Solonina, Abstr., 1900, i, 147).—Dibenzenesulphonamides, $NR(SO_2Ph)_2$, formed from primary amines, are converted into benzenesulphonamides, $NHR\cdot SO_2Ph$, when warmed with sodium ethoxide in alcoholic solution. Benzenesulphonamides derived from primary aliphatic or hydrocyclic amines, containing more than

6 carbon atoms, are insoluble in aqueous alkali hydroxides, and react with sodium in ethereal solution to form sodium derivatives, which are insoluble in ether. Benzenesulphonamides derived from secondary amines are soluble in ether and are not acted on by sodium. Hinsberg's method for the separation of primary and secondary amines is modified accordingly.

Dibenzenesulphonethylamide, $NEt(SO_2Ph)_2$, crystallises in needles and melts at 81—82°. *Benzenesulphonheptadecylamide* crystallises in glistening needles and melts at 62—63°. *Benzenesulphon*-o-*xylidide* crystallises in colourless prisms and melts at 118°. *Dibenzenesulphon*-o-*xylidide* crystallises in needles and melts at 155°. *Dibenzenesulphon*-p-*xylidide* crystallises in needles and melts at 186—187°. *Benzenesulphon-ψ-cumidide* crystallises in glistening, colourless leaflets and melts at 136—137°. *Dibenzenesulphon-ψ-cumidide* crystallises in thin, white needles and melts at 186—187°.

Benzenesulphonethyl-p-*xylidide*, formed by heating benzenesulphon-*p*-xylidide with ethyl iodide and sodium ethoxide in alcoholic solution, crystallises in stellate groups of white needles, melts at 70°, and is hydrolysed by concentrated hydrochloric acid to *ethyl*-p-*xylidine*; this is a refractive oil, which has an odour resembling naphthalene, becomes dark on exposure to air, and boils at 222—223° under 748 mm. pressure. *Tetrabenzenesulphon*-m-*phenylenediamide*, $C_6H_4[N(SO_2Ph)_2]_2$, crystallises in glistening, silver leaflets and melts at 217°. *Tetrabenzenesulphon*-p-*phenylenediamide* crystallises in needles and melts at 235—236°. *Benzenesulphon*-m-*toluidide* forms a white, crystalline crust and melts at 80°. G. Y.

Action of Sulphur on Aniline and Aniline Hydrochloride. Oscar Hinsberg (*Ber.*, 1905, **38**, 1130—1137. Compare Hofmann, Abstr., 1895, i, 87).—The product obtained on fusing a mixture of aniline, aniline hydrochloride, and sulphur contains diphenylamine, dithioaniline, Merz and Weith's thioaniline, and a thioaniline which melts at 58°. Hofmann's thioaniline, melting at 85·5°, was probably a mixture.

Dithioaniline (diaminophenyl disulphide) crystallises in yellow prisms or slender needles, melts at 76—77°, is easily soluble in alcohol, benzene, or ether, and is reduced by zinc dust and hydrochloric acid to aminophenyl mercaptan. The hydrochloride forms a crystalline powder; the diacetyl derivative, $(NHAc\cdot C_6H_4)_2S_2$, crystallises in small needles, melts at 182°, and when boiled with zinc dust and aqueous sodium hydroxide dissolves, and on acidification yields a precipitate, which is probably acetylaminophenyl mercaptan.

Thioaniline (*op*-diaminophenyl sulphide) (Nietzki and Bothof, Abstr., 1897, i, 36), which melts at 58°, crystallises in slender needles or stellate groups of glistening needles, is easily soluble in alcohol, ether, or benzene, and with lead peroxide in alcoholic hydrochloric acid solution gives a violet coloration. The *hydrochloride*, $C_{12}H_{12}N_2S,2HCl$, crystallises in thick prisms or stellate groups of needles; the *sulphate*, $(C_{12}H_{12}N_2S)_2,H_2SO_4$, crystallises from water; the *oxalate*,

$$C_{12}H_{12}N_2S,C_2H_2O_4,$$

crystallises in nodular aggregates of needles. The *diacetyl* derivative,

$C_{16}H_{16}O_2N_2S$, crystallises in slender needles, and when heated with concentrated sulphuric acid yields a product which is soluble in aqueous alkali hydroxide. G. Y.

Phenylcarbimide as a Reagent for determining the Constitution of Tautomeric Compounds. HEINRICH GOLDSCHMIDT (*Ber.*, 1905, **38**, 1096—1098).—A reply to Michael (this vol., i, 195). G. Y.

ω-Sulphomethyl Derivatives of Aromatic Amines. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 156760).—Diphenamine compounds, prepared by the combination of formaldehyde (1 mol.) with an aromatic amine (2 mols.) (Eberhardt and Welter, Abstr., 1894, i, 451; Eibner, Abstr., 1899, i, 41), react with sodium hydrogen sulphite to form ω-sulphomethyl derivatives of the amines, according to the equation:

$$(R\cdot NX)_2CH_2 + H\cdot SO_3Na = R\cdot NX\cdot CH_2\cdot SO_3Na + R\cdot NHX,$$

where R = aryl, X = hydrogen or alkyl. The products are identical with those obtained from methyleneaniline and its derivatives (Abstr., 1903, i, 336).

*Sodium ω-sulphomethyl-*p*-toluidine*, $C_6H_4Me\cdot NH\cdot CH_2\cdot SO_3Na$, from methylenedi-*p*-toluidine, forms glistening, white leaflets.

The *sodium* salt of *ω-sulphomethylethylaniline*, from the methylene compound, $CH_2(C_6H_5Et)_2$, crystallises in glistening leaflets. Potassium cyanide forms *ω-cyanomethylethylaniline*, a colourless oil, converted by concentrated sulphuric acid into the *amide*, melting at 114—115°. Ammonium sulphide forms the *thioamide* melting at 140°; hydroxylamine forms the *amidoxime*, melting at 72°.

Sodium hydrogen ω-sulphomethylanthranilate, from methylenedianthranilic acid, forms yellowish-white needles or leaflets. C. H. D.

Action of Diphenylamine on Nitric Acid. ISIDORE BAY (*Compt. rend.*, 1905, **140**, 796—797).—The intense blue coloration which diphenylamine sulphate gives with nitric acid is also obtained with a large number of other oxidising agents. Diphenylamine and other analogous aromatic amines are to be regarded as the leuco-bases of the coloured oxidation products. H. M. D.

New Additive Products of Tetrahydrobenzene. LÉON BRUNEL (*Bull. Soc. chim.*, 1905, [iii], **33**, 382—384. Compare Abstr., 1903, i, 157).—When *cyclo*hexene, dissolved in ether, is treated with acid anhydrides in presence of mercuric oxide and iodine, esters of α-iodohydroxy*cyclo*hexane (*loc. cit.*) are formed. The *acetate*, $C_6H_{10}I\cdot OAc$, is an aromatic, faintly yellow liquid, has a sp. gr. 1·61 at 0°, and decomposes when distilled even under reduced pressure. The *propionate*, $C_2H_5\cdot CO_2\cdot C_6H_{10}I$, resembles the acetate and has a sp. gr. 1·54 at 0°.

This reaction is regarded as taking place in two stages, thus: $Ac_2O + HgO + I_2 + C_6H_{10} = C_6H_{10}I\cdot OAc + HgI\cdot OAca$ and $HgI\cdot OAc + I_2 + C_6H_{10} = C_6H_{10}I\cdot OAc + HgI_2$, and if insufficient iodine is used the intermediate mercury acetoiodide may be isolated. The mercuric salt of

the appropriate organic acid may be used in place of the acid anhydride. T. A. H.

Crystalline Double Compounds of Phenols with Alkali Phenoxides. CURT GENTSCH (D.R.-P. 156761 and 157616).—Phenols are known to dissolve in solutions of alkali phenoxides. It is found that crystalline double compounds may be prepared by adding dry alkali carbonate or hydroxide to a solution of the phenol in an indifferent solvent and boiling the mass with benzene or alcohol, from which the compound crystallises on cooling. The *compound* from phenol and potassium phenoxide, $C_6H_5{\cdot}OK,3C_6H_5{\cdot}OH$, forms glistening needles and melts at 106—108°. The *p*-cresol *compound*,

$$C_6H_4Me{\cdot}OK,3C_6H_4Me{\cdot}OH,$$

melts at 146—147°, the corresponding *compound* from *m*-cresol melts at 88°. The ortho- and meta-compounds dissolve more readily in benzene than the para-compound, and the method may thus be used for the separation of the isomeric cresols. C. H. D.

2-Hydroxydibenzyl. STANISLAUS VON KOSTANECKI, A. ROST, and WLADISLAUS SZABRAŃSKI (*Ber.*, 1905, **38**, 943—944).—2-*Methoxydibenzyl*, $OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2Ph$, obtained by reducing 2-methoxystilbene with sodium and alcohol, is a colourless oil distilling at 295°, and when heated with hydriodic acid yields 2-*hydroxydibenzyl*, which crystallises from dilute alcohol in colourless plates melting at 81°. Ethyl bromoacetate reacts with an alcoholic solution of the sodium derivative of 2-hydroxydibenzyl, yielding crude *ethyl* 2-*dibenzylyloxyacetate*, $CH_2Ph{\cdot}CH_2{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}CO_2Et$, and this is readily hydrolysed to the *acid*, $C_{16}H_{16}O_3$, which crystallises from dilute alcohol in large, colourless needles melting at 137°. J. J. S.

Derivatives of the Pentamethylene Series. JULIUS VON BRAUN and ADOLPH STEINDORFF (*Ber.*, 1905, **38**, 956—966. Compare Abstr., 1904, i, 731, 918).—$\alpha\epsilon$-*Diphenoxypentane*, $OPh{\cdot}[CH_2]_5{\cdot}OPh$, obtained by the action of sodium phenoxide on $\alpha\epsilon$-dichloro-, dibromo- or di-iodo-pentane, forms colourless crystals, melts at 48—49°, and boils at 215—217° under 12 mm. and at about 340° under the ordinary pressure. It is best prepared from the crude $\alpha\epsilon$-dichloropentane obtained from the action of phosphorus pentachloride on benzoylpiperidine, containing much benzonitrile. When the diphenyl ether is heated with hydrobromic acid at 170°, it gives $\alpha\epsilon$-dibromopentane, whilst by using hydriodic acid, $\alpha\epsilon$-di-iodopentane, boiling at 135—136° under 12 mm. pressure, is obtained in nearly theoretical yield (compare Hamonet, Abstr., 1904, i, 643).

α-*Chloro* ϵ-*phenoxypentane*, $CH_2Cl{\cdot}[CH_2]_4{\cdot}OPh$, prepared by converting benzoyl-ϵ-iodopentylamine, $NHBz{\cdot}[CH_2]_5{\cdot}I$, into benzoyl-$\epsilon$-phenoxypentylamine by means of sodium phenoxide and distilling the crude product with phosphorus pentachloride, boils at 155° under 15 mm. and at 283—285° under the ordinary pressure, undergoing in the latter case a slight decomposition; it is also obtained by the action of sodium phenoxide on $\alpha\epsilon$-dichloropentane. α-*Iodo*-ϵ-*phenoxypentane*, prepared by boiling the chloro-derivative with alcoholic sodium iodide, boils at

172—179° under 12 mm. pressure. *α-Bromo-ε-phenoxypentane*, prepared from αε-dibromopentane and sodium phenoxide, boils at 162—163° under 12 mm. pressure. α-Chloro-ε-phenoxypentane is only slowly attacked by potassium cyanide, but α-bromo- and α-iodo-phenoxypentanes are readily converted into *α-cyano-ε-phenoxypentane*, which crystallises from a mixture of ether and light petroleum in long prisms and melts at 36°. *ε-Phenoxyhexoic acid*, $OPh{\cdot}[CH_2]_5{\cdot}CO_2H$, obtained by hydrolysing the nitrile, crystallises from light petroleum as a white powder and melts at 71°; the *silver* salt was analysed. The *amide*, $OPh{\cdot}[CH_2]_5{\cdot}CO{\cdot}NH_2$, formed together with the acid in the hydrolysis of the nitrile, crystallises from dilute alcohol in white leaflets and melts at 99°. W. A. D.

Indirect Fermentative Oxidations. Course of the Reaction in the Oxidation of Quinol. L. Marchadier (*J. Pharm. Chim.*, 1905, [vi], 21, 299—302. Compare Bourquelot and Marchadier, Abstr., 1904, ii, 552).—The oxidation of a solution of quinol, with or without the addition of hydrogen peroxide, is greatly accelerated by the addition of a 20 per cént. extract of bran containing toluene and glycerol. Quinone and quinhydrone are formed, and finally the brown products resulting from the oxidation of quinone are obtained. The relative proportions of quinone and quinol in the mixture obtained are dependent on the amount of ferment used. G. D. L.

Action of Bromine and Chlorine on Phenols; Substitution-products, ψ-Bromides and ψ-Chlorides. Tetrachloro-*p*-dihydroxytolane. Theodor Zincke and H. Wagner (*Annalen*, 1905, **338**, 236—258. Compare Abstr., 1902, i, 282).—*Tetrachlorodihydroxytolane*, $OH{\cdot}C{\lessgtr}\genfrac{}{}{0pt}{}{CCl{\cdot}CH}{CCl{:}CH}{\gtrless}C{\cdot}C{:}C{\cdot}C{\lessgtr}\genfrac{}{}{0pt}{}{CH{\cdot}CCl}{CH{:}CCl}{\gtrless}C{\cdot}OH$, is prepared from tetrachlorodihydroxystilbene, which is acetylated by acetic anhydride in the presence of sulphuric acid, and then converted into the dibromide by bromine in acetic acid solution; the latter yields the tolane derivative when it is heated with a solution of sodium ethoxide in absolute alcohol; the tolane melts at 225—226°. In the last process, tetrachlorodihydroxyhydrobenzoin diethyl ether (m. p. 186°) is formed, and can be isolated by acidifying the alkaline mother liquor.

*Tetrachloro-*p*-dihydroxydeoxybenzoin*,

$$OH{\cdot}C{\lessgtr}\genfrac{}{}{0pt}{}{CCl{\cdot}CH}{CCl{:}CH}{\gtrless}C{\cdot}CH_2{\cdot}CO{\cdot}C{\lessgtr}\genfrac{}{}{0pt}{}{CH{\cdot}CCl}{CH{:}CCl}{\gtrless}C{\cdot}OH,$$

prepared by warming tetrachloro-*p*-dihydroxytolane with concentrated sulphuric acid, crystallises in needles melting at 249°; its *diacetyl* derivative crystallises in prisms melting at 158—159°.

In its action on tetrachlorodihydroxytolane, bromine differs from chlorine in that only two, and not four, atoms are taken up, the *dibromide*, $C_2Br_2\left(C{\lessgtr}\genfrac{}{}{0pt}{}{CH{\cdot}CCl}{CH{:}CCl}{\gtrless}C{\cdot}OH\right)_2$, being formed; it crystallises in needles melting and decomposing at 268°, and dissolves in sodium hydroxide with a bluish-violet coloration, acids precipitating a red compound. Prolonged treatment with alkali hydroxide re-

generates the tolane. The *diacetyl* derivative crystallises in needles melting at 212°.

The *quinone* of tetrachlorotolanedibromide,

$$C_2Br_2\left(C{<}{}^{CH:CCl}_{CH:CCl}{>}CO\right)_2,$$

prepared by oxidising the dibromide in the presence of acetic acid by nitric or chromic acids or manganese dioxide, crystallises in yellow plates, becoming red at 235—240°, but not molten at 280°; by boiling with acetic acid and sodium acetate, it can be converted into the tetrachloro-*p*-dihydroxybenzil, and when heated with an acetic acid solution of hydrogen bromide into tetrachloro-*p*-dihydroxytolane dibromide. Treatment with an acetic acid solution of hydrogen chloride converts the quinone into a *ψ-chloride*, $C_2Cl_2Br_2\left(CH{<}{}^{CH:CCl}_{CH:CCl}{>}CO\right)_2$, which crystallises in needles becoming yellow at 120—130°, and melts and decomposes at 222—223°; on heating, it loses 2HBr, yielding a hexachloro-compound (m. p. 248°), and on treatment with a solution of hydrogen chloride in acetic acid it loses HCl and HBr, a stilbene chlorobromide being formed, which on warming with acetic acid or acetone passes into the *quinone*,

$$CO{<}{}^{CCl:CH}_{CCl:CH}{>}C:CCl\cdot CBr:C{<}{}^{CH:CCl}_{CH:CCl}{>}CO;$$

the latter crystallises in reddish-yellow prisms or needles melting and decomposing at 218—219°. It is reduced by stannous chloride in acetic acid solution to *tetrachloro*-p-*dihydroxytolane chlorobromide*, which crystallises in needles melting at 258—259°; its *diacetyl* derivative melts at 191°.

Hydrogen chloride in acetic acid solution forms an additive product, *tetrachloro*-p-*dihydroxystilbene chloride*,

$$OH\cdot C{\lessgtr}{}^{CCl\cdot CH}_{CCl:CH}{\gtrless}C\cdot CCl:CH\cdot C{\lessgtr}{}^{CH\cdot CCl}_{CH:CCl}{>}C\cdot OH,$$

with the tolane derivative, the additive product with 2 mols. of hydrogen chloride, tetrachloro-*p*-dihydroxydibenzyl-*ψ*-chloride, being formed at the same time; the stilbene derivative crystallises in needles melting at 197°, and is converted into a quinone by nitric acid and into the original tetrachloro-*p*-dihydroxytolane by boiling with alkalis. The *diacetyl* derivative forms prismatic needles melting at 162°. The corresponding *stilbene bromide* is formed together with the analogous dibromodibenzyl derivative when hydrogen bromide is substituted for hydrogen chloride, and crystallises in needles melting at 185°; its *diacetyl* derivative crystallises in needles sintering at 132° and melting at 136—137°.

Tetrachloro-*p*-dihydroxytolane is readily oxidised by all agents to a red compound, which is best prepared by using potassium ferricyanide in alkaline solution; the compound, which is taken to be the *quinhydrone*, $O{<}{}^{C_6H_2Cl_2(OH):C:C:C_6H_2Cl_2(OH)}_{C_6H_2Cl_2 \text{———} C:C \text{——} C_6H_2Cl_2}{>}O$, corresponding with tetrachlorotolanequinone, crystallises in red needles or plates melting at 202—207°, and dissolves in alkali hydroxides with a blue coloration; from this solution, the compound is precipitated unchanged, but on keeping is converted into the original tetrachlorodihydroxytolane. K. J. P. O.

[*p*-**Methoxyphenylethylcarbinol.**] AUGUST KLAGES (*Ber.*, 1905, 38, 912—914. Compare Abstr., 1902, i, 609).—A reply to Hell and Hofmann (this vol., i, 58). The author has repeated the preparation of *p*-methoxyphenylethylcarbinol and confirms his previous statements (*loc. cit.*) in all details.

If anisaldehyde and magnesium ethyl bromide are allowed to react in the cold and the mixture treated with ice and dilute sulphuric acid, the main product obtained is the *ether* of methoxyphenylethylcarbinol, $(OMe\cdot C_6H_4\cdot CHEt)_2O$, which is a colourless, viscid oil; it boils at 215—216° under 17 mm. pressure, and has a sp. gr. 1·057 at 17°/4°, and n_D 1·5394 at 17°. G. Y.

p-**Methylaminobenzoic Acid.** MAX JAFFÉ (*Ber.*, 1905, 38, 1208—1212. Compare Abstr., 1905, ii, 186).—The identity of the supposed *p*-methylaminobenzoic acid, isolated from the urine of animals fed on *p*-dimethylaminobenzaldehyde, has been established by its preparation synthetically by the action of methyl iodide, potassium hydroxide and methyl alcohol on *p*-aminobenzoic acid. So obtained, it crystallises in colourless or faintly yellow needles, melting at 155—157°, and gives no precipitate on the addition of lead acetate to the aqueous solution; it forms an emerald-green, crystalline *copper* salt, a bluish-green, amorphous *basic copper* salt and a colourless *silver* salt crystallising in microscopic needles. The *nitroso*-derivative separates from alcohol in glistening, yellow needles melting at 195—196°. An acid melting at 228—229° has been described by Houben as *p*-methylaminobenzoic acid (Abstr., 1904, i, 1014).
E. F. A.

Compounds of Formaldehyde with the Amides of Monobasic Acids. ALFRED EINHORN (D.R.-P. 157355).—Formaldehyde condenses with amides in the presence of acid condensing agents to form diacyl derivatives of methylenediamine, such as methylenedibenzamide. When alkaline condensing agents are employed, however, compounds having the general formula $R\cdot CO\cdot NH\cdot CH_2\cdot OH$ are obtained.

Hydroxymethylbenzamide, $COPh\cdot NH\cdot CH_2\cdot OH$, crystallises from acidified water in hexagonal tablets and melts at about 104—106°; it dissolves in alcohol, ethyl acetate, benzene, or chloroform, sparingly in water. *Hydroxymethyl*-p-*toluamide* crystallises from alcohol in needles and melts at 102—104°. *Hydroxymethylsalicylamide* crystallises from water in prismatic needles and melts at 128°; *hydroxymethyl*-p-*hydroxybenzamide* forms white needles, melts at 155°, and reduces ammoniacal silver solution. *Hydroxymethyl*isovaler*amide* forms felted needles and melts at 69—71°; *hydroxymethylguaiacolacetamide*, from guaiacoxylacetamide, forms felted needles and melts at 80°. Asparagine yields a highly condensed product. C. H. D.

Acyl Derivatives of Benzylamine. ALFRED EINHORN (D.R.-P. 156398).—The hydroxymethyl derivatives of amides react with a large number of aromatic compounds in presence of condensing agents to form acyl derivatives of benzylamine. In a few cases, when acids are employed, methylenediamides are also produced.

Hydroxymethylbenzamide, $C_6H_5 \cdot CO \cdot NH \cdot CH_2 \cdot OH$, from benzamide and formaldehyde, crystallises from benzene or chloroform, melts at 104—106°, and dissolves sparingly in water, readily in alcohol. It condenses with *p*-nitrophenol to form *benzoyl*-m-*nitro*-o-*hydroxybenzylamine*, melting at 217—218°. *Hydroxymethylchloroacetamide* crystallises from acetone in leaflets and melts at 97—99°. It condenses with *p*-nitrophenol in presence of cold concentrated sulphuric acid to form *chloroacetyl*-m-*nitro*-o-*hydroxybenzylamine*,

$$NO_2 \cdot C_6H_3(OH) \cdot CH_2 \cdot NH \cdot CO \cdot CH_2Cl,$$

which crystallises from alcohol in needles and melts at 182°.

Dihydroxymethylsuccinamide forms crystalline aggregates and melts and decomposes at 158°. It condenses with *p*-nitrophenol to form the *compound* $C_2H_4[CO \cdot NH \cdot CH_2 \cdot C_6H_3(NO_2) \cdot OH]_2$, crystallising in small, white needles which become yellow on separating from nitrobenzene and melting at 257°. The *compound*

$$OH \cdot C_{10}H_6 \cdot CH_2 \cdot NH \cdot COPh,$$

from hydroxymethylbenzamide, β-naphthol, and hydrochloric acid, crystallises from alcohol in prisms and melts at 185—186°. *Benzoylbenzylaminecarboxylic acid*, $COPh \cdot NH \cdot CH_2 \cdot C_6H_4 \cdot CO_2H$, from hydroxymethylbenzamide and benzoic acid, melts at 190°. The *compound* from hydroxymethylchloroacetamide and benzoic acid forms needles and melts at 176°; the corresponding *compound* from salicylic acid melts at 196°. The *compound* from hydroxymethylchloroacetamide and acetanilide forms prisms and melts at 206°. Benzene condenses with dihydroxymethylsuccinamide in presence of sulphuric acid to form the *compound* $C_6H_4 \Big< \begin{matrix} CH_2 \cdot NH \cdot CO \cdot CH_2 \\ CH_2 \cdot NH \cdot CO \cdot CH_2 \end{matrix}$, an amorphous, yellow substance, which becomes brown at 200° and melts and decomposes at about 225°. The same amide condenses with β-naphthol to form a *compound* melting at 222—224°, and with *m*-xylene-4-sulphonic acid to form a white, crystalline *compound* which remains unmelted at 260°. C. H. D.

Diphenylsulphone-*o*-carboxylic Acid and Related Compounds. WILLIAM S. WEEDON and HOWARD W. DOUGHTY (*Amer. Chem. J.*, 1905, **33**, 386—430. Compare Graebe and Schultess, Abstr., 1891, 1058).—By the action of dilute nitric acid on phenylthiosalicylic acid, Graebe and Schultess obtained a substance which they termed "sulphobenzide-*o*-carboxylic acid" and assigned the formula

$$C_6H_5 \cdot SO_2 \cdot C_6H_4 \cdot CO_2H.$$

On repeating this work, it has been found that the product of the reaction consists almost entirely of *diphenylsulphoxide*-o-*carboxylic acid*, $C_6H_5 \cdot SO \cdot C_6H_4 \cdot CO_2H$, which crystallises from methyl alcohol in long, colourless prisms, melts at 163°, and is readily soluble in alcohol or chloroform and sparingly so in ether or hot water; it crystallises from water with $1H_2O$. The *barium*, *strontium*, and *calcium* salts are described.

When phenylthiosalicylic acid is treated with fuming nitric acid, a product is obtained which has the melting point of the substance described by Graebe and Schultess. This product, however, is not a single substance, but a mixture of diphenylsulphoxide-*o*-carboxylic acid and a nitro-derivative of this acid.

Nitrodiphenylsulphoxide-o-*carboxylic acid*, $NO_2 \cdot C_6H_4 \cdot SO \cdot C_6H_4 \cdot CO_2H$,

separates from hot benzene in small, colourless crystals and melts at 222° (corr.); its *barium* salt is described. The yield of this acid is increased by boiling the phenylthiosalicylic acid with fuming nitric acid. When phenylthiosalicylic acid is heated with a mixture of fuming nitric acid and sulphuric acid, a product is obtained which is probably a mixture of di- and tri-nitrophenylsulphoxide-*o*-carboxylic acids together with some of the mononitro-compound.

By the action of potassium permanganate on phenylthiosalicylic acid, *diphenylsulphone-*o*-carboxylic acid*, $C_6H_5\cdot SO_2\cdot C_6H_4\cdot CO_2H$, is produced, which crystallises from benzene in white needles, melts at 146°, and is very soluble in alcohol, ether, glacial acetic acid, or acetone; when crystallised from water, it is obtained as efflorescent prisms with $1\cdot 5H_2O$ and melts at 51·5°. This compound is not identical with the *o*-phenylsulphonebenzoic acid described by Canter (Abstr., 1901, i, 208). The *calcium*, *barium*, and *strontium* salts of diphenylsulphone-*o*-carboxylic acid are described. The *chloride* crystallises in colourless prisms or needles and melts at 80° (corr.); the *amide* forms white, slender needles and melts at 175—175·5° (corr.); the *anhydride* separates from hot alcohol in small, colourless crystals and melts at 148° (corr.). The *ethyl* ester crystallises in feathery needles and melts at 78—79° (corr.); the *methyl* ester separates from methyl alcohol in rectangular plates and melts at 63°. When diphenylsulphone-*o*-carboxylic acid is heated with concentrated sulphuric acid, benzophenonesulphone is produced, which is identical with the compound obtained by Graebe and Schultess by the oxidation of thioxanthone with chromic acid.

When phenylthiosalicylic acid is heated with lime, phenyl sulphide is produced. If diphenylsulphone-*o*-carboxylic acid is treated in a similar manner, diphenylsulphone is obtained.

When phenyl *o*-tolyl sulphide is oxidised with potassium permanganate, diphenylsulphone-*o*-carboxylic acid is produced.

By the oxidation of phenyl-*o*-tolylsulphone with potassium permanganate, Canter (*loc. cit.*) obtained a compound which he supposed to be diphenylsulphone-*o*-carboxylic acid. On repeating his experiments, it has been found that the product is not diphenylsulphone-*o*-carboxylic acid, but is the isomeric *p*-phenylsulphonebenzoic acid first described by Newell (Abstr., 1898, i, 430). The formation of this compound under the conditions of Canter's investigation is due to the presence of *p*-toluenesulphonic chloride in the *o*-toluenesulphonic chloride used in the preparation of the phenyl-*o*-tolylsulphone. When, however, pure phenyl-*o*-tolylsulphone is treated with potassium permanganate, diphenylsulphone-*o*-carboxylic acid is the sole product of the reaction.

p-*Phenylsulphidebenzoic acid*, $C_6H_5\cdot S\cdot C_6H_4\cdot CO_2H$, prepared by the action of thiophenol on the solution obtained by the diazotisation of *p*-aminobenzoic acid, crystallises from alcohol in colourless, hexagonal plates and melts at 177° (corr.); its *barium* salt is described. On oxidation with potassium permanganate, it is converted into *p*-phenylsulphonebenzoic acid, which melts at 277° (corr.); the *barium* salt was prepared and analysed. *p*-Phenylsulphonebenzoyl chloride melts at 146—147° (corr.), and the amide melts at 248·3—248·8° (corr.).

E. G.

Reaction between Unsaturated Compounds and Organic Magnesium Compounds. V. Reactions with α-Cyanocinnamic Acid. ELMER P. KOHLER and MARIE REIMER (*Amer. Chem. J.*, 1905, **33**, 333—356. Compare Abstr., 1904, i, 595; this vol., i, 207, 208).—Ethyl α-cyanocinnamate can be prepared in theoretical yield by a slight modification of the method described by Carrick (Abstr., 1892, 1086). When a solution of this ester in ether or benzene is added to a boiling solution of magnesium phenyl bromide, a magnesium compound is obtained which, on decomposition with water, yields *ethyl α-cyano-ββ-diphenylpropionate*, $CHPh_2\cdot CH(CN)\cdot CO_2Et$, which crystallises from alcohol in large, colourless pyramids, melts at 78°, and is readily soluble in chloroform, acetone, or hot alcohol, and fairly so in ether or cold alcohol. *α-Cyano-ββ-diphenylpropionic acid* crystallises in small, colourless needles, melts at 162°, and is very soluble in alcohol or ether and slightly so in light petroleum or hot water. When the acid is heated at 190°, it undergoes decomposition with evolution of carbon dioxide and formation of *ββ-diphenylpropionitrile*, $CHPh_2\cdot CH_2\cdot CN$, which crystallises in small, lustrous prisms, melts at 100°, and is readily soluble in most organic solvents. *ββ-Diphenylpropionamide* crystallises in needles, melts at 127°, and is readily soluble in alcohol or ether and very slightly so in water. *ββ-Diphenylmethylmalonamic acid*, $CHPh_2\cdot CH(CO_2H)\cdot CO\cdot NH_2$, obtained by boiling ethyl cyanodiphenylpropionate with aqueous potassium hydroxide and acidifying the product, crystallises in long, slender needles and is readily soluble in alcohol and moderately so in ether; its melting point depends largely on the rate of heating, since the substance easily suffers decomposition with evolution of carbon dioxide and formation of diphenylpropionamide; when heated for a short time at 150°, it is decomposed completely.

Ethyl α-bromo-α-cyano-ββ-diphenylpropionate,

$$CHPh_2\cdot CBr(CN)\cdot CO_2Et,$$

obtained by the action of bromine on the magnesium compound formed by adding magnesium phenyl bromide to ethyl α-cyanocinnamate, crystallises in large, colourless prisms, melts at 97°, and is readily soluble in chloroform or acetone and moderately so in alcohol or ether. On hydrolysis with potassium hydroxide, the ester is converted into *α-cyano-ββ-diphenylcinnamic acid*, $CPh_2\!:\!C(CN)\cdot CO_2H$, which crystallises in needles, melts at 178°, decomposes above 190°, and is readily soluble in alcohol, ether, or chloroform, and sparingly so in light petroleum or hot water; when boiled with alcoholic potassium hydroxide, a small quantity of ββ-diphenylcinnamic acid is produced, together with a larger proportion of *ββ-diphenylcinnamonitrile*, $CPh_2\!:\!CH\cdot CN$, which forms long, pale yellow needles and melts at 49°.

When the magnesium compound is treated with a solution of acetyl chloride in benzene, a *compound*, $(C_7H_8O_3N)_2Mg,2H_2O$, is obtained which crystallises in small, lustrous prisms, and, when treated with dilute hydrochloric acid, is converted into ethyl cyanoacetate. The filtrate from this substance yields a crystalline *compound*,

$$CHPh_2\cdot C(CN)\!:\!C(OEt)\cdot O\cdot CHPh_2,$$

which melts at 156°, is not decomposed at 300°, and is readily soluble in chloroform or hot glacial acetic acid; when heated with concentrated

hydrochloric acid for 8 hours at 225°, it is decomposed with formation of benzhydrol ether, diphenylpropionic acid, alcohol, carbon dioxide, and ammonia; the same substance can be prepared by treating the magnesium compound with diphenylbromomethane.

By the action of benzoyl chloride on the magnesium compound, magnesium ethyl cyanobenzoylacetate is produced together with the compound just described, which melts at 156°.

By the action of magnesium α-naphthyl bromide on ethyl α-cyanocinnamate, *ethyl α-cyano-β-phenyl-β-naphthylpropionate*,

$$C_{10}H_7\cdot CHPh\cdot CH(CN)\cdot CO_2Et,$$

is produced, which crystallises in minute plates, melts at 132°, and is readily soluble in chloroform or ethyl acetate. *β-Phenyl-β-naphthylmethylmalonamic acid*, $C_{10}H_7\cdot CHPh\cdot CH(CO_2H)\cdot CO\cdot NH_2$, obtained by boiling the ester with alcoholic potassium hydroxide, decomposes at 170—180°, and on oxidation is converted into α-naphthophenone.

When ethyl α-cyanocinnamate is treated with magnesium methyl iodide, ethyl α-cyano-β-phenylbutyrate is produced. *α-Cyano-β-phenylbutyric acid*, $CHPhMe\cdot CH(CN)\cdot CO_2H$, crystallises in colourless prisms, melts at 130°, decomposes at 180°, and is readily soluble in alcohol, ether, or chloroform, and sparingly so in light petroleum. *β-Phenylethylmalonamic acid*, $CHPhMe\cdot CH(CO_2H)\cdot CO\cdot NH_2$, crystallises in needles and melts and decomposes at 172°; when heated at 180°, it is converted into *β-phenylbutyramide*, which forms white, slender needles, melts at 105°, and is very soluble in alcohol or ether. *β-Phenylbutyric acid*, $CHPhMe\cdot CH_2\cdot CO_2H$, was obtained as an oil by hydrolysing the amide; its *sodium* salt is described.

By the action of magnesium benzyl chloride on ethyl α-cyanocinnamate, an oily ester was obtained which, on boiling with alcoholic potassium hydroxide, was converted into *βγ-diphenylethylmalonamic acid*, $CH_2Ph\cdot CHPh\cdot CH(CO_2H)\cdot CO\cdot NH_2$, which crystallises in slender needles, melts and decomposes at about 182°, and is oxidised by potassium permanganate with formation of deoxybenzoin. *βγ-Diphenylbutyramide*, $CH_2Ph\cdot CHPh\cdot CH_2\cdot CO\cdot NH_2$, crystallises in thick, long needles and melts at 62°.

When ethyl α-cyanocinnamate is treated with magnesium *iso*propyl bromide, an oily product is obtained which, on hydrolysis with potassium hydroxide, is converted into the *compound* $C_{13}H_{19}O_3N$, which crystallises in slender needles and melts and decomposes at 176°.

By the action of magnesium phenylacetylene bromide on ethyl α-cyanocinnamate, the *ester*, $CPh\vdots C\cdot CHPh\cdot CH(CN)\cdot CO_2Et$, is obtained, which crystallises in colourless needles, melts at 80°, and is readily soluble in hot alcohol and moderately so in cold alcohol or ether. E. G.

Constitution of the so-called Hagemann's Ester. Paul Rabe and Fritz Rahm (*Ber.*, 1905, **38**, 969—973).—Hagemann's ester, obtained by the action of methylene iodide on ethyl sodioacetoacetate (Abstr., 1893, i, 393), is *ethyl 2-methyl*cyclo-*Δ²-hexene-4-one-1-carboxylate*, $CO_2Et\cdot CH{<}{\begin{smallmatrix}CMe\colon CH\\ CH_2\cdot CH_2\end{smallmatrix}}{>}CO$, and not the β-ketonic ester, $CO_2Et\cdot CH{<}{\begin{smallmatrix}CO-CH\\ CH_2\cdot CH_2\end{smallmatrix}}{>}CMe$, as supposed by Callenbach (Abstr.,

1897, i, 271). That this is so is shown by the fact that it is obtained from ethyl 6-methyl*cyclo*hexane-6-ol-4-one-1 : 3-dicarboxylate, $CO_2Et\cdot CH<\genfrac{}{}{0pt}{}{CH_2\cdot CH(CO_2Et)}{CMe(OH)-CH_2}>CO$ (Abstr., 1904, i, 747), by the elimination of water and one carbethoxyl group under the influence of sodium ethoxide, and by its giving ethyl 4-hydroxy-2-methylbenzoate (Claisen, Abstr., 1897, i, 592) under the action of bromine in carbon disulphide solution. Both the "acid" and "neutral" esters of Hagemann give the same result in the latter case and both give also the same *semicarbazone*, $C_{11}H_{17}O_3N_3$, which crystallises from alcohol in slender, white needles melting at 169°. The relationship between these substances will be considered in a future paper.

W. A. D.

Constitution of the *cyclo*Hexenonecarboxylic Esters. Georg Merling [with Robert Welde and Aladar Skita] (*Ber.*, 1905, **38**, 979—985).—On reducing ethyl *iso*phoronecarboxylate [ethyl 2 : 6 : 6-trimethyl*cyclo*-Δ^2-hexene-4-one-1-carboxylate] (Abstr., 1903, i, 317) with sodium and alcohol, a mixture of three pairs of *cis-trans*-isomeric hydroxy-acids of the formula

$$CO_2H\cdot CH<\genfrac{}{}{0pt}{}{CMe_2-CH_2}{CHMe\cdot CH_2}>CH\cdot OH$$

is obtained ; on heating these acids with dilute sulphuric acids, three stable *lactones*, melting respectively at 44°, 58°, and 39°, are formed, showing that in the parent ketonic acid the carboxyl and carbonyl groups occupy a para-position relatively to each other. The lactones are oxidised by Beckmann's solution to three stereoisomeric *keto-dihydrocyclogeranic acids* or *dihydroisophoronecarboxylic acids*, $CO_2H\cdot CH<\genfrac{}{}{0pt}{}{CMe_2-CH_2}{CHMe\cdot CH_2}>CO$, melting at 123—124°, 127—128°, and 118—119° respectively, which boil at 178—179° under 11 mm. pressure and lose carbon dioxide when heated above 200°; this fact proves them to be para- and not ortho-ketonic acids.

Ethyl *iso*phoronecarboxylate (2 : 6 : 6-trimethyl*cyclo*-Δ^2-hexene-4-one-1-carboxylate) is stable towards boiling dilute sulphuric acid, but by boiling aqueous barium hydroxide is resolved into carbon dioxide, alcohol, and *iso*phorone. The ester exists in two modifications, one soluble and the other insoluble in aqueous alkalis ; the former is probably the enolic modification, $CO_2Et\cdot CH<\genfrac{}{}{0pt}{}{CMe_2\cdot CH}{CMe=CH}>C\cdot OH$.

Knoevenagel's dimethyl*cyclo*hexenonecarboxylic esters (*Annalen*, 1894, **281**, 109) are also probably δ-ketonic esters ; on reduction with sodium and alcohol, a mixture of stereoisomeric *hydroxy-acids*,

$$CO_2H\cdot CH<\genfrac{}{}{0pt}{}{CHMe\cdot CH_2}{CHMe\cdot CH_2}>CH\cdot OH,$$

is obtained, which has not yet been resolved into its constituents ; on oxidation, the mixed acids give a mixture of ketonic acids having the formula $CO_2H\cdot CH<\genfrac{}{}{0pt}{}{CHMe\cdot CH_2}{CHMe\cdot CH_2}>CO$; this mixture is not decomposed when distilled at 169—174° under 10 mm. pressure, and the acids therefore belong to the δ-ketonic and not to the β-ketonic series. The

original ethyl dimethyl*cyclo*hexenone-carboxylate is therefore

$$CO_2Et\cdot CH<\begin{matrix}CHMe\cdot CH_2\\CHMe{=}CH\end{matrix}>CO.$$

Similar considerations would apply to the so-called Hagemann's ester, which is therefore a δ-ketonic ester (compare Rabe and Rahm, this vol., i, 348).

In conclusion, the nature of the condensation of ethyl sodioacetoacetate with ethyl *iso*propylideneacetoacetate is discussed.

W. A. D.

Oxidation of Indigo by Potassium Permanganate. N. CHOLIN (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 1521—1524).—It has been observed that, if synthetical crystalline indigotin is converted into indigotindisulphonic acid and then oxidised to sulphoisatin by means of potassium permanganate solution, the amount of the latter used up is less by about 13 per cent. than that calculated from the equation: $C_{16}H_{10}O_2N_2 + O_2 = C_{16}H_{10}O_4N_2$. The author finds that this is not due to a portion of the indigotin undergoing oxidation during the sulphonation, thus: $C_{16}H_{10}O_2N_2 + 2H_2SO_4 = C_{16}H_{10}O_4N_2 + 2SO_2 + 2H_2O$, as has been suggested.

On treating a cooled solution of indigotin in carbon tetrachloride with 4 mols. of chlorine or bromine, the theoretical quantity of halogen is absorbed, but further investigation shows that the product consists (when bromine is employed) of a mixture of unaltered indigotin with the mono-, $C_{16}H_9O_2N_2Br$, and di-bromo-derivatives, $C_{16}H_8O_2N_2Br_2$.

T. H. P.

Synthesis of Iodogorgonic Acid. HENRY L. WHEELER and GEORGE S. JAMIESON (*Amer. Chem. J.*, 1905, **33**, 365—372. Compare Henze, Abstr., 1903, i, 668).—It is shown that iodogorgonic acid is a di-iodotyrosine, probably 3 : 5-di-iodotyrosine,

$$OH\cdot C_6H_2I_2\cdot CH_2\cdot CH(NH_2)\cdot CO_2H,$$

and that it can be prepared by adding rather less than the calculated quantity of iodine to a solution of *l*-tyrosine in presence of alkali hydroxide. The substance is soluble in water at 25° to the extent of 0·2 per cent., but is much more soluble in hot water. By the action of hydriodic acid, or of zinc and hydrochloric acid, it is converted into tyrosine. Di-iodotyrosine *hydrochloride* and *sulphate*, and the *silver*, *copper*, and *lead* salts are described; the *acetyl* derivative forms a yellow powder which is sparingly soluble in alcohol and decomposes at about 225°.

E. G.

4-*p*-Hydroxyphenylsalicylic Acid. J. FAURE (*Bull. Soc. chim.*, 1905, [iii], **33**, 348—351).—4-p-*Hydroxyphenylsalicylic acid*, $OH\cdot C_6H_4\cdot C_6H_3(OH)\cdot CO_2H$, prepared by Tiemann and Reimer's method (Abstr., 1877, i, 77), using *p*-diphenol as a starting point, separates from boiling dilute alcohol in small, colourless crystals, melts at 225°, dissolves in water to the extent of 0·22 and 4·4 per cent. at 19° and 98° respectively, is readily soluble in chloroform, ether, or warm alcohol, and gives a yellow coloration with calcium hypochlorite and blue with ferric chloride. When heated with lime, it loses carbon dioxide and

forms diphenol. The *sodium*, *potassium*, *ammonium*, *calcium*, *magnesium*, *zinc*, *nickel*, *cobalt*, and *lead* salts were prepared.

T. A. H.

Cinnamylidenelævulinic Acid and its Reduction Products. HANS RUPE and FELIX SPEISER (*Ber.*, 1905, 38, 1113—1125. Compare this vol., i, 220).—*Cinnamylidenelævulic acid*,

$CHPh:CH\cdot CH:CH\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H$,

is formed when cinnamaldehyde and lævulic acid are heated with pyridine in a reflux apparatus at 144—155° for 24 hours. It crystallises in large, transparent, highly refractive, yellow crystals, melts at 161°, and is easily soluble in most organic solvents. The *silver*, *copper*, *barium*, *calcium*, $(C_{14}H_{13}O_3)_2Ca,4H_2O$, and *magnesium* salts are described. The *ethyl* ester, $C_{16}H_{18}O_3$, crystallises in long, green needles and melts at 82°; the *methyl* ester crystallises in yellow leaflets and melts at 88°. With hydroxylamine in alkaline solution, cinnamylidenelævulic acid forms an *oximidoximic acid*,

$CHPh:CH\cdot CH(NH\cdot OH)\cdot CH_2\cdot C(N\cdot OH)\cdot CH_2\cdot CH_2\cdot CO_2H$,

which crystallises in delicate yellow leaflets, decomposes at 130°, and dissolves in aqueous sodium hydroxide on warming. The *tetrabromide*, $C_{14}H_{14}O_3Br_4$, formed by the action of bromine on the acid in chloroform solution, crystallises from alcohol and melts at 203°; the *ethyl* ester, $C_{16}H_{18}O_3Br_4$, crystallises in glistening, white needles and melts at 152°.

Cinnamylidenelævulic acid is reduced by sodium amalgam in dilute sulphuric acid solution to trans-*γ-keto-η-phenyl-Δ^ε-octenoic acid*,

$CH_2Ph\cdot CH:CH\cdot CH_2\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H$,

which crystallises in large, colourless prisms, melts at 96°, is easily soluble in most organic solvents, decolorises alkaline potassium permanganate solution, and when boiled with aqueous alkali carbonates yields a volatile oil. The *salts* are mostly easily soluble in water, and on concentration of their solutions are decomposed with evolution of carbon dioxide; the *silver* salt, $C_{14}H_{15}O_3Ag$, is very sensitive to light. The *ethyl* ester, $C_{14}H_{15}O_3Et$, is a yellow oil which boils at 203° under 14 mm. pressure, and under the atmospheric pressure distils with slight decomposition; the *methyl* ester is an oil which boils at 204—205° under 16 mm. pressure. With hydrogen bromide in glacial acetic acid solution, the acid forms *ε-bromo-γ-keto-η-phenyloctoic acid*, $CH_2Ph\cdot CH_2\cdot CHBr\cdot CH_2\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H$, which crystallises in long, colourless prisms, melts at 79°, and rapidly decomposes in a vacuum, less rapidly on exposure to the air. With hydroxylamine in aqueous solution, the unsaturated keto-acid forms an *oxime*,

$C_{14}H_{17}O_3N$,

which crystallises in slender needles and melts at 122°. 1-*Phenyl*-5-*styrylpyrazoline*-3-*propionic acid*,

$CHPh:CH\cdot C_3N_2H_3Ph\cdot CH_2\cdot CH_2\cdot CO_2H$,

is formed by the action of phenylhydrazine on the hydrobromide of the keto-acid; it crystallises in slender, white needles, melts at 138°, is easily soluble in alcohol, ether, benzene, or cold aqueous sodium carbonate solution, and with ferric chloride or potassium dichromate in acid solution gives transitory violet to purple and red colorations.

When treated with bromine in a neutral solvent, the *trans*-acid forms a dibromide, which, when warmed with concentrated aqueous potassium carbonate solution, is converted into cis-γ-*keto*-η-*phenyl*-Δ^{ϵ}-*octenoic acid.* This crystallises in thick, colourless plates or long, transparent, triclinic (?) prisms, melts and changes into the *trans*-acid at 71°, is easily soluble in the usual organic solvents, and decolorises potassium permanganate. The *barium* and *calcium* salts are easily soluble in water; the *alkali* salts decompose on concentration of their aqueous solutions; the white, unstable *silver* salt crystallises in white needles. The *oxime* of the *cis*-acid crystallises in nacreous leaflets and melts at 120—121°. With hydrogen bromide in glacial acetic acid, the *cis*-acid yields the same hydrobromide as is obtained from the *trans*-acid. α-*Phenyl*-Δ^{β}-*hepten*-ϵ-*one*, $CH_2Ph \cdot CH \colon CH \cdot CH_2 \cdot CO \cdot CH_2Me$, is formed along with the *cis*-acid by the action of aqueous potassium carbonate on the dibromide of the *trans*-acid. It is an oil which distils with partial decomposition at 230—236° under 14 mm. pressure, is insoluble in aqueous potassium carbonate, and forms a *semicarbazone*, $C_{14}H_{19}ON_3$, crystallising in glistening, white, silky needles. G. Y.

2-Methoxystilbene. CASIMIR FUNK and STANISLAUS VON KOSTANECKI (*Ber.*, 1905, **38**, 939—940).—2-*Methoxystilbene*-β-*carboxylic acid*, $OMe \cdot C_6H_4 \cdot CH \colon CPh \cdot CO_2H$, is readily obtained by the condensation of phenylacetic acid with salicylaldehyde methyl ether according to Oglialoro's method; it crystallises from alcohol in colourless needles, melts at 186—187°, and when distilled yields α-phenylcoumarin.

2-*Methoxystilbene* may be obtained by leaving the acid in contact with hydriodic acid of sp. gr. 1·96 for several days. It crystallises from dilute alcohol in plates melting at 70°.

3-*Methoxystilbene*-β-*carboxylic acid* melts at 189° and does not yield 3-methoxystilbene when treated in a similar manner. J. J. S.

Stilbene Derivatives. STANISLAUS VON KOSTANECKI and J. SULSER (*Ber.*, 1905, **38**, 941—942. Compare preceding abstract).—Three isomeric acids, $OMe \cdot C_6H_4 \cdot CH \colon C(CO_2H) \cdot C_6H_3 <^{O}_{O}> CH_2$, have been obtained by condensing sodium homopiperonalate with the three isomeric methoxybenzaldehydes in the presence of acetic anhydride at 150—170°.

2-*Methoxy*-3′ : 4′-*methylenedioxystilbene*-β-*carboxylic acid* crystallises in small needles and melts at 225—226°; the isomeric 3-*methoxy*-compound forms stout needles and melts at 204—205°, and the 4-*methoxy*-derivative melts at 199—200°. The acids lose carbon dioxide when kept for several days in closed vessels with concentrated hydriodic acid.

2-*Methoxy*-3′ : 4′-*methylenedioxystilbene*,

$$OMe \cdot C_6H_4 \cdot CH \colon CH \cdot C_6H_3 <^{O}_{O}> CH_2,$$

crystallises in prisms and melts at 99—100°; the isomeric 4-*methoxy*-derivative melts at 153—154°, but the 3-methoxy-compound has not been isolated.

2 : 4-*Dimethoxystilbene*-β-*carboxylic acid*, $C_6H_3(OMe)_2 \cdot CH \colon CPh \cdot CO_2H$,

melts at 196—198°, and 2 : 4-*dimethoxy-3′ : 4′-methylenedioxystilbene-β-carboxylic acid*, $C_6H_3(OMe)_2\cdot CH\cdot C(CO_2H)\cdot C_6H_3{<}^{O}_{O}{>}CH_2$, melts at 203°. J. J. S.

Products of the Condensation of Opianic Acid. DANIEL BRUNS (*Arch. Pharm.*, 1905, **243**, 49—57).—Meconinedimethylketone,

$$\begin{matrix} CH{=\!=}CH{-\!-}C\cdot CH(CH_2Ac) \\ C(OMe){:}C(OMe)\cdot C{-\!-\!-}CO \end{matrix}{>}O \quad \left(= R''{<}^{CH(CH_2Ac)}_{CO}{>}O\right),$$

is obtained when opianic acid is allowed to react with acetone, CH_3Ac, in the presence of an alkali, and the product is acidified (Goldschmiedt, Abstr., 1892, 179; Hemmelmayr, Abstr., 1894, i, 151; compare also Book, Abstr., 1902, i, 464); in neutral and acid solutions, no condensation occurs. The substance does really behave like a lactone, for it reacts slowly with an alkali instead of neutralising at once as much as would correspond with the isomeric acid $CHAc{:}CH\cdot R''\cdot CO_2H$. The lactone of which it is derivative, $R''{<}^{CH(OH)}_{CO}{>}O$, is a tautomeric form of the aldehyde acid, $CHO\cdot R''\cdot CO_2H$, and stands to it in the same relation as the carbinol form to the aldehydic form of a ψ-ammonium base (this vol., i, 368). The true methyl ester of opianic acid, $CHO\cdot R''\cdot CO_2Me$ (Wegscheider, Abstr., 1893, i, 167), does not condense with acetone.

A compound of opianic acid with chloroform could not be obtained. C. F. B.

Condensation of Aminobenzoic Acids with Ethyl Malonate. WALTER VON POLLACK (*Monatsh.*, 1905, **26**, 327—334. Compare Schiff, Abstr., 1886, 549).—When heated together without a solvent, at 165—170°, anthranilic acid and ethyl malonate form o-*malonaminobenzoic acid*, $CH_2(CO\cdot NH\cdot C_6H_4\cdot CO_2H)_2$, which crystallises in slender, white needles and melts and decomposes at 242°. p-*Malonaminobenzoic acid*, obtained in the same manner, decomposes at 276°. The *o*- and *p*-acids distil, with partial decomposition, in a vacuum, and are easily soluble in concentrated sulphuric acid, from their solutions in which they are precipitated unchanged on addition of water. *m*-Malonaminobenzoic acid, formed in the same manner as its isomerides, decomposes at 258—259°.

These acids form crystalline salts, of which the *sodium* ($+3H_2O$) and *silver* salts of the *o*- and the *silver* salts of the *p*-acid were analysed. The *o*- and *p*-acids form crystalline *diphenylhydrazones*, $C_{29}H_{26}O_4N_6$, which decompose above 360°. On addition of hydrochloric acid to the cooled aqueous alkaline solution of potassium nitrite and *o*-malonaminobenzoic acid, the *dinitroso*-derivative, $C_{17}H_{12}O_8N_4$, is obtained as a yellow, flocculent precipitate, which decomposes above 350°.

When heated at their melting points, the three malonaminobenzoic acids lose carbon dioxide and form similar, brown, tarry products. G. Y.

Methylated Tannin. JOSEF HERZIG and RUDOLF TSCHERNE (*Ber.*, 1905, **38**, 989—991).—*Methyl tannin*, prepared by the action of diazomethane on an ethereal solution of tannin, separates from ethyl alcohol as a colourless, amorphous powder and melts at 124—126°. Its probable composition is represented by $C_{24}H_8O_7(OMe)_8$ or $C_{25}H_{10}O_7(OMe)_8$. Gallic acid is produced by the action of hydriodic acid on it. Methyl tannin is dextrorotatory. When heated with potassium hydroxide, it forms a mixture of trimethyl gallic acid and dimethyl gallic acid (3 : 4 : 5-trimethoxybenzoic and 5-hydroxy-3 : 4-dimethoxybenzoic acids). A. McK.

Characterisation of Aromatic Aldehydes and Ketones. PAVEL IW. PETRENKO-KRITSCHENKO and F. DOLGOPOLOFF (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 1505—1509. Compare Petrenko-Kritschenko and Eltschaninoff, Abstr., 1903, i, 440; Petrenko-Kritschenko and Kestner, Abstr., 1903, ii, 719; Kldiaschwili, Abstr., 1903, ii, 719).—The authors have measured the velocities of the reactions of a number of aldehydes and ketones with phenylhydrazine and with potassium hydrogen sulphite, the results showing that aromatic ketones react considerably more slowly than the corresponding aliphatic compounds, whilst with aldehydes the reverse is the case. Investigation of the effect produced on the speed of the reaction by the introduction of methylene groups shows that closed-chain compounds, to which Baeyer's tension theory attributes a ring-angle greater than a right angle (namely, rings with 5, 6, 7, or 8 members), exhibit velocities of reaction less than those of the corresponding open-chain compounds. Where this angle is less than a right angle, the reverse holds.

The authors explain the difference in behaviour between aromatic ketones and aldehydes by supposing that in both cases the symmetry of the benzene nucleus is disturbed, the ring-angle for the ketones approximating to the magnitude of the angle of a 7- or 8-atom ring, whilst in the case of aromatic aldehydes the ring-angle is diminished to approximately the value it possesses in a tetramethylene ring.

T. H. P.

Oxidation of Benzaldehyde in the presence of Acetic Anhydride. WILLEM P. JORISSEN and WILHELM E. RINGER (*Chem. Centr.*, 1905, i, 817—818; from *Chem. Weekblad*, **2**, 19—39).—When a mixture of benzaldehyde (1 mol.) and acetic anhydride (2 mols.) with or without admixture of sand is exposed in diffused light and in a closed vessel to an atmosphere of oxygen, benzoyl acetyl peroxide is obtained. In opposition to the observation of Baeyer and Villiger (Abstr., 1900, i, 437), the compound is only slowly resolved on warming with 10 per cent. sodium hydroxide into benzoyl peroxide. When the mixture is exposed to air in a dish with small surface, oxidation is slow and benzoic acid is formed, whilst in larger dishes benzoyl acetyl peroxide is also produced.

Diffused daylight greatly accelerates the oxidation without, however, a period of induction or after-effect. The light from a Welsbach burner is inactive, but the electric arc is extraordinarily active, a

marked after-effect, but no period of induction, being noticed. When passed through a red glass plate, the electric light is inactive, but when passed through a violet plate is again active, showing both a period of induction and after-effect. Magnesium light similarly accelerates the oxidation with a short period of induction and more prolonged after-effect, but when allowed to pass through the space in which the mixed vapours are present, no effect is noticed, owing probably to the small vapour pressure of the aldehyde. Röntgen and radium rays are inactive. G. D. L.

Preparation of Aldehydes. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 157573).—Alkyl formates react with 2 mols. of magnesium alkyl haloids to form secondary alcohols or their formic esters (Grignard, Abstr., 1901, i, 679). When, however, at least 2 mols. of alkyl formate are employed for each 2 mols. of magnesium alkyl or aryl haloid, aldehydes are obtained. For example, $MgBrPh + H\cdot CO_2Et = OEt\cdot CHPh\cdot O\cdot MgBr$. This intermediate compound either decomposes directly into benzaldehyde and $MgBr\cdot OEt$, or possibly reacts with water according to the equation: $OEt\cdot CHPh\cdot O\cdot MgBr + H_2O = MgO + HBr + OEt\cdot CHPh\cdot OH$, this alcoholate then decomposing into alcohol and benzaldehyde. In addition to the above example, the preparation of propaldehyde from ethyl iodide and amyl formate, of *iso*valeraldehyde from *iso*amyl bromide and ethyl formate, and of phenylacetaldehyde from benzyl chloride and methyl formate by means of the magnesium compounds is described. C. H. D.

*cyclo***Butanone.** NIC. M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 106—109).—*Tetramethylenecarboxylic bromamide*,

$$CH_2<\begin{matrix}CH_2\\CH_2\end{matrix}>CBr\cdot CO\cdot NH_2,$$

prepared by brominating tetramethylenecarboxylic acid and treating the bromo-anhydride thus obtained with ammonia, crystallises from aqueous alcohol in long, flat needles, melts at 153°, and dissolves readily in water or benzene.

cyclo*Butanone*, $CH_2<\begin{matrix}CH_2\\CH_2\end{matrix}>CO$, obtained by the action of bromine and potassium hydroxide on the preceding bromide, has an odour resembling that of acetone, boils at 99—101°, has the sp. gr. 0·9344 at 18°/18°, and n_D 1·4214 at 18°; it is soluble in water, gives a crystalline compound with sodium hydrogen sulphite, and yields a *semicarbazone* separating from alcohol in plates melting at 221°. Oxidation with concentrated nitric acid gives succinic acid.

1 : 1-*Dibromo*cyclo*butane*, $CH_2<\begin{matrix}CH_2\\CH_2\end{matrix}>CBr_2$, boils at 159—161° and has the sp. gr. 1·8934 at 20°/20°; when treated with semicarbazide hydrochloride and potassium acetate, it is converted into the semicarbazone of *cyclo*butanone. T. H. P.

Inversion of ψ-Ionone and its Derivatives. PAUL ALEXANDER (D.R.-P. 157647).—A certain quantity of resin is always formed in the inversion of ψ-ionone and its derivatives by acids. A better result

is obtained by heating the compound to be inverted with water or alcohol at 170—190°, with or without the addition of salts, such as the chlorides, acetates, or sulphates of the alkalis or alkaline earths.

ψ-Iononecarboxylic esters give an almost theoretical yield of ionone when heated with water under pressure; ψ-ionone gives a 50 per cent. yield of ionone with sodium acetate. In this case, it is advisable to separate the inverted product and repeat the operation, as ionone is less stable at high temperatures than ψ-ionone. C. H. D.

Formation of Additive Compounds from Hydroxylamine and Arylsulphonacetonitriles. JULIUS TRÖGER and FRANZ VOLKMER (*J. pr. Chem.*, 1905, [ii], 71, 236—248. Compare foregoing abstract; Tiemann and Krüger, Abstr., 1884, 1325; 1885, 790).—Arylsulphonacetonitriles form amidoximes when warmed with hydroxylamine hydrochloride and sodium carbonate in concentrated aqueous-alcoholic solution.

Phenylsulphonethenylamidoxime, $SO_2Ph\cdot CH_2\cdot C(NH_2)\colon NOH,\frac{1}{2}H_2O$ (or sometimes with H_2O), forms glistening, white prisms or leaflets and melts at 158°. p-*Tolylsulphonethenylamidoxime* crystallises in white leaflets or needles and melts and decomposes at 190—192°. It may also be obtained in granular crystals, which sinter at 190° and melt and decompose at about 196°. o-*Tolylsulphonethenylamidoxime* forms a white powder and melts at about 104°. 1:3-Xylyl-4-sulphonacetonitrile melts at 79—80°. 1:3-*Xylyl-4-sulphonethenylamidoxime* forms a white, woolly, crystalline mass and melts and decomposes at 142°. ψ-*Cumylsulphonacetonitrile*, formed from sodium ψ-cumenesulphinate and chloroacetonitrile, crystallises in long, glistening needles and melts at 110—111°. ψ-*Cumylsulphonethenylamidoxime* crystallises in glistening, white leaflets and melts at 146°. α-*Naphthylsulphonethenylamidoxime* forms small, glistening, granular crystals and melts and decomposes at about 206°. β-*Naphthylsulphonethenylamidoxime* crystallises in matted, glistening needles and melts and decomposes at 170—175°. m-*Phenylenedisulphondiethenylamidoxime* forms a white, crystalline powder and decomposes when strongly heated. p-*Chlorophenylsulphonethenylamidoxime* crystallises in glistening, white leaflets and melts and decomposes at 202°. p-*Bromophenylsulphonethenylamidoxime* crystallises in glistening, white leaflets and melts and decomposes at 198°. Potassium *p*-iodobenzenethiosulphonate, formed by the action of potassium sulphide on *p*-iodobenzenesulphonic chloride in warm concentrated aqueous solution, is converted by potassium cyanide in concentrated aqueous solution into potassium *p*-iodobenzenesulphinate. *p*-Iodobenzenesulphinic acid melts at about 160° (compare Abstr., 1902, i, 274). p-*Iodophenylsulphonethenylamidoxime* crystallises in white leaflets and melts and decomposes at 176°.

o-*Anisolesulphonacetonitrile*, $OMe\cdot C_6H_4\cdot SO_2\cdot CH_2\cdot CN$, crystallises in glistening, white prisms and melts at 84—85°. o-*Anisolesulphonethenylamidoxime* forms a white, crystalline powder and melts at 105°. p-*Anisolesulphonacetonitrile* crystallises in colourless, glistening needles and melts at 115°. p-*Anisolesulphonethenylamidoxime* crystallises in stellate groups of slender needles and melts at 116°.

p-*Phenetolesulphonacetonitrile* crystallises in needles and melts at

140—141°. p-*Phenetolesulphonethenylamidoxime* forms a white, crystalline powder and melts and decomposes at 175°. G. Y.

Ketonic Fission of Carbinols. GEORG VON GEORGIEVICS (*Ber.*, 1905, **38**, 884—886. Compare Fischer and Hess, this vol., i, 205).—Pararosaniline reacts with hydrogen peroxide in slightly alkaline solution to form 4 : 4′-diaminobenzophenone, which melts at 244° (m. p. 237°, Wichelhaus, Abstr., 1889, 781). In the same manner, crystal-violet yields tetramethyldiaminobenzophenone, which melts at 175° (compare Fehrmann, Abstr., 1888, 156; Graebe, Abstr., 1888, 158). G. Y.

Condensation of Imines with Ketones and Nitromethane. CHARLES MAYER (*Bull. Soc. chim.*, 1905, [iii], **33**, 395—399. Compare Abstr., 1904, i, 832, and this vol., i, 214).—*Anilinophenylethyl* iso*propyl ketone*, $NHPh\cdot CHPh\cdot CH_2\cdot COPr^{\beta}$, obtained by the action of benzylideneaniline on methyl *iso*propyl ketone dissolved in alcohol, crystallises in brilliant needles, melts at 119—120°, and dissolves readily in benzene, ether, or boiling alcohol. *Anilinophenylethyl butyl ketone* crystallises in leaflets, melts at 80°, and when dissolved in acetic or sulphuric acid and the solution poured on ice furnishes *benzylidenemethyl butyl ketone*, $CHPh\colon CH\cdot CO\cdot C_4H_9$, which forms colourless lamellæ and melts at 40°. The *products* obtained by the condensation of benzylideneaniline with methyl *p*-tolyl and methyl *m*-tolyl ketones melt at 173° and 172° respectively, resemble anilinobenzylacetophenone in solubility (Tambor and Wilde, Abstr., 1898, i, 313), and on solution in sulphuric acid furnish the corresponding ketones; the *cinnamenyl*-m-*tolyl ketone* so obtained, crystallises from methyl alcohol in slightly yellow prisms and melts at 73°. *Anilinobenzyl-lævulic acid*, $NHPh\cdot CHPh\cdot CH_2\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H$, melts at 148°, is readily soluble in acetone, less so in alcohol, ether, and benzene, and on solution in sulphuric acid yields benzylidenelævulic acid (Erlenmeyer, Abstr., 1904, i, 500). The ethyl ester of the imino-acid crystallises in needles, melts at 93—94°, and is hydrolysed by sulphuric acid to *ethyl benzylidenelævulate*, $CHPh\colon CH\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2Et$, which crystallises in silky needles and melts at 44—45° (compare Erdmann, Abstr., 1890, 495).

Anilinophenylnitroethane, $NHPh\cdot CHPh\cdot CH_2\cdot NO_2$, obtained by the action of nitromethane on benzylideneaniline forms large, colourless rhombohedra, melts at 90°, is readily soluble in ether, benzene, and warm alcohol, and when warmed with hydrochloric acid yields aniline and β-nitrostyrene. A mixture of benzaldehyde, acetone, piperidine, and alcohol, after being left for 45 days, yielded dibenzylideneacetone.

The author's results show that in order that a ketone may condense with benzylideneaniline it must contain a methyl group and must not contain a quaternary carbon atom next the carbonyl group. Condensation as a rule does not occur between ketones and imines possessing stable hydrochlorides, for example, benzylidene-*p*-phenetidine. Methyl cyanide and quinaldine do not condense with imines, in spite of their analogy with the methyl ketones. T. A. H.

Dibenzylideneacetone and Triphenylmethane. VIII. ADOLF BAEYER [in part with RICHARD HALLENSLEBEN] (*Ber.*, 1905, **38**, 1156—1164. Compare Abstr., 1903, i, 811; 1904, i, 308 and 898; this vol., i, 281).—*p*-Tri-iodotriphenylcarbinol, when purified by removing the azo-compounds which contaminate it by means of alcoholic-ethereal stannous chloride, is quite colourless and melts at 162—163°.

When concentrated sulphuric acid is mixed with a solution of *p*-trichlorotriphenylcarbinol in chloral and chloroform is then added, the *sulphate*, $C_{19}H_{12}Cl_3\cdot SO_4H,H_2SO_4$, separates in brown prisms or needles with a greenish-blue surface lustre. The *sulphate*,

$$C_{19}H_{12}I_3\cdot SO_4H,H_2SO_4,$$

of *p*-tri-iodotriphenylcarbinol is obtained in a similar manner and forms microscopic, brown crystals. The production of diacid salts from these weak bases is probably due to the employment of the concentrated sulphuric acid, which, it is suggested, consists of a dimolecularly associated acid, "dimolsulphuric acid."

p-Trichlorotriphenylcarbinyl chloride gives with stannic chloride in chloroform solution the *stannichloride*, $C_{19}H_{12}Cl_4,SnCl_4$, which forms red crystals with a blue surface colour; the *stannichloride*,

$$C_{19}H_{12}I_3Cl,SnCl_4,$$

derived from *p*-tri-iodotriphenylcarbinyl chloride, is a crimson, crystalline powder with a green, metallic lustre.

p-*Trichlorotriphenylcarbinyl ethyl ether*, $C_{21}H_{17}OCl_3$, crystallises from chloroform on adding alcohol in lustrous prisms and melts at 182°; p-*tri-iodotriphenylcarbinyl ethyl ether* forms small, white prisms and melts at 223°.

p-Trianisylcarbinol gives rise to two sulphates:

$$(1)\ C_{22}H_{21}O_3\cdot SO_4H,H_2SO_4,$$

obtained by means of chloral and precipitating with ethyl acetate, forms orange-yellow needles; (2) $(C_{22}H_{21}O_3\cdot SO_4H)_2,H_2SO_4$, probably a mixture of $C_{22}H_{21}O_3\cdot SO_4H$ and $C_{22}H_{21}O_3\cdot SO_4H,H_2SO_4$ obtained by adding sulphuric acid mixed with chloroform to a solution of the carbinol in chloroform, forms crimson crystals.

m-Trianisylcarbinol gives only the *salt* $(C_{22}H_{21}O_3\cdot SO_4H)_2,H_2SO_4$ when sulphuric acid is mixed with its solution in chloral, ethyl acetate being subsequently added.

The colour of some triphenylcarbinol salts is discussed from the standpoint of the "carbonium" theory and of "halochromy."

W. A. D.

Action of Organo-magnesium Compounds on Cinnamylideneacetophenone. ELMER P. KOHLER (*Ber.*, 1905, **38**, 1203—1208. Compare this vol., i, 207, 208, 215).—*β-Phenyl-β-styrylpropiophenone* (*γ-benzylidene-β-phenylbutyrophenone*), $COPh\cdot CH_2\cdot CHPh\cdot CH{:}CHPh$, prepared by the action of magnesium phenyl bromide on cinnamylideneacetophenone, melts at 93°. Its solution in concentrated sulphuric acid is intensely red. Its constitution was determined by the isolation of benzoic acid and *β*-benzoyl-*α*-phenylpropionic acid as products of its oxidation by potassium permanganate. Its *oxime* separates from alcohol in needles and melts at 129°; its *dibromide*

separates from a mixture of chloroform and light petroleum in glistening prisms and melts at 171°.

β-Benzyl-β-styrylpropiophenone (*γ-benzylidene-β-benzylbutyrophenone*), $COPh\cdot CH_2\cdot CH(CH_2Ph)\cdot CH:CHPh$, prepared by the action of magnesium benzyl chloride on cinnamylideneacetophenone, melts at 125°. That the substance is a ketone and not a tertiary alcohol, as indicated by Bauer, was proved by the formation of benzoic acid and β-benzoyl α-benzylpropionic acid as its oxidation products. *β-Benzoyl-α-benzylpropionic acid*, $COPh\cdot CH_2\cdot CH(CH_2Ph)\cdot CO_2H$, separates from alcohol in needles and melts at 176°.

β-Benzyl-β-styrylpropiophenone dibromide separates from a mixture of alcohol and chloroform in glistening prisms and melts at 152°.

β-Benzyl-β-styrylpropiophenone oxime separates from a mixture of ether and light petroleum in needles and melts at 144°.

β-Styryl-β-ethylpropiophenone (*γ-benzylidene-β-ethylbutyrophenone*), $COPh\cdot CH_2\cdot CHEt\cdot CH:CHPh$, prepared by the action of magnesium ethyl bromide on cinnamylideneacetophenone, is identical with the product described by Bauer as "diphenylmethylhexadienol," but is not a tertiary alcohol, since it yields benzoic acid and β-benzoyl-α-ethylpropionic acid on oxidation. Its *dibromide* separates from a mixture of alcohol and chloroform in prisms and melts at 142°. Its *oxime* separates from light petroleum in needles and melts at 91°.

A. McK.

Action of Zinc Chloride on Acid Esters of Phenols. II. 2 : 4-Dihydroxy-1 : 5-diacetylbenzene. JOHAN F. EIJKMAN, F. BERGEMA, and I. T. HENRARD (*Chem. Centr.*, 1905, i, 814—817; from *Chem. Weekblad*, 2, 59—72 and 79—93. Compare Abstr., 1904, i, 664).—2 : 4-Dihydroxy-1 : 5-diacetylbenzene is best prepared by warming resorcinol diacetate with zinc chloride; it forms colourless needles melting at 183° (corr.), sparingly soluble in cold, more readily in warm organic solvents, and is identical with the "*iso*resacetophenone" of Claus and Huth (Abstr., 1896, i, 227). By the action of alkyl iodides or bromides on the potassium salt, simple and mixed ethers are formed. Those of the type $C_6H_2Ac_2(OR^I)(OR^{II})$ are identical independently of the order of introduction of the groups R^I and R^{II}, thus proving the orientation of the parent substance. The dioximes of the ethers as a rule crystallise from alcohol or benzene in slender needles. 2 : 4-*Dihydroxy*-1 : 5-*diacetylbenzene dioxime* melts at 242°. An excess of potassium permanganate oxidises the dimethyl and diethyl esters of 2 : 4-dihydroxy-1 : 5-diacetylbenzene to 4 : 6-*dimethoxy*- and 4 : 6-*diethoxy*-iso*phthalic acids*, separating from alcohol in crystals, sparingly soluble in water, and melting and decomposing at 266° and 250° respectively. The dimethyl ether with seven atomic proportions of oxygen gives 3-*carboxy*-4 : 6-*dimethoxyphenylglyoxylic acid*,

$$CO_2H\cdot C_6H_2(OMe)_2\cdot CO\cdot CO_2H,$$

as colourless needles melting and decomposing at 243°.

2 : 4-Dihydroxy-1 : 5 diacetylbenzene condenses with benzaldehyde, yielding the *monobenzylidene* derivative, which forms bright yellow needles melting at 192°, and the *dibenzylidene* derivative, which crystallises from benzene in reddish-yellow needles and melts at 202°,

whilst with anisaldehyde the corresponding *dianisylidene* compound, which separates from benzene in golden-yellow needles and melts at 204°, is produced. By the action of benzaldehyde and hydrogen chloride on the solution of the dibenzylidene compound in alcohol and a little benzene, *tetrabenzylideneflavindogenide*,

$$\begin{array}{l} \quad\quad\quad\quad\quad CHPh{\cdot}O{\cdot}C{:}CH{\cdot}C{\cdot}O—CHPh \\ CHPh{:}C—CO—C{:}CH{\cdot}C{\cdot}CO{\cdot}C{:}CHPh \end{array},$$

is obtained; it separates from benzene in yellow crystals, melts at 257°, and dissolves in boiling dilute alkalis to a yellow, and in sulphuric acid to a cherry-red, solution.

The constants of the following *ethers* of 2 : 4 dihydroxy-1 : 5-acetylbenzene and their oximes are given, the melting points being corrected: *monomethyl*, m. p. 121·5°, sp. gr. 1·1297, and n_a 1·52932 at 134·7°; *oxime*, m. p. 274°; *monoethyl*, m. p. 109°, sp. gr. 1·1120, and n_a 1·52876 at 109·1°; *oxime*, m. p. 217°; *monopropyl*, m. p. 94·5°, sp. gr. 1·0821, and n_a 1·51989 at 112·4°; *oxime*, m. p. 186°; *mono*iso*propyl*, m. p. 97·5°; *oxime*, m. p. 162°; *monobutyl*, m. p. 63°, sp. gr. 1·0860, and n_a 1·52690 at 78·8°; *oxime*, m. p. 170°; *mono*iso*butyl*, m. p. 88°; *oxime*, m. p. 213°; *dimethyl*, m. p. 171·5°; *oxime*, m. p. 255°; *diethyl*, m. p. 156°; *oxime*, m. p. 245°; *dipropyl*, m. p. 86°, sp. gr. 1·0173, and n_a 1·50150 at 131·1°; *oxime*, m. p. 206°; *di*iso*propyl*, m. p. 126·5°; *oxime*, m. p. 235°; *dibutyl*, m. p. 92·5°, sp. gr. 0·9893, and n_a 1·49324 at 110·8°; *oxime*, m. p. 169°; *di*iso*butyl*, m. p. 99°; *oxime*, m. p. 207°; *methylethyl*, m. p. 152°; *oxime*, m. p. 241°; *methylpropyl*, m. p. 125·5°; *oxime*, m. p. 237°; *methyl*iso*propyl*, m. p. 97°; *oxime*, m. p. 235°; *methylbutyl*, m. p. 117°; *oxime*, m. p. 189°; *methyl*iso*butyl*, m. p. 102·5°; *oxime*, m. p. 210°; *ethylpropyl*, m. p. 95°; *oxime*, m. p. 218°; *ethyl*iso*propyl*, m. p. 101·5°; *oxime*, m. p. 235°; *ethylbutyl*, m. p. 104°; *oxime*, m. p. 193°; *ethyl*iso*butyl*, m. p. 72°; *oxime*, 195°; *propyl*iso*propyl*, m. p. 78°; *oxime*, m. p. 220°; *propylbutyl*, m. p. 61·5°; *oxime*, m. p. 176°; *propyl*iso*butyl*, m. p. 64°; *oxime*, m. p. 200°; iso*propylbutyl*, m. p. 76°; *oxime*, m. p. 196°; iso*propyl*iso*butyl*, m. p. 80°; *oxime*, m. p. 211°; *butyl*iso*butyl*, m. p. 78°; *oxime*, m. p. 187°.

2 : 4-Dihydroxy-1 acetylbenzene has a sp. gr. 1·1800 and n_a 1·56467 at 141·1°; the following constants for some of its ethers are given: 4-*methyl*, m. p. 50°, sp. gr. 1·1310, and n_a 1·54322 at 81·2°; 4-*ethyl*, m. p. 48°, sp. gr. 1·0866, and n_a 1·53082 at 80°; 4-*propyl*, m. p. 25°, sp. gr. 1·0553, and n_a 1·52128 at 80·1°; 4-*butyl*, m. p. 42°, sp. gr. 1·0333, and n_a 1·51479 at 79·7°; *dimethyl*, m. p. 40°, sp. gr. 1·0914, and n_a 1·52476 at 80·1°; *diethyl*, m. p. 68°, sp. gr. 1·0266, and n_a 1·50627 at 80·7°; *dipropyl*, m. p. 26°, sp. gr. 0·9928, and n_a 1·49758 at 79·5°; *dibutyl*, m. p. 32°, sp. gr. 0·9678, and n_a 1·49029 at 80°; 4-*ethyl*-2-*methyl*, m. p. 44°, sp. gr. 1·0562, and n_a 1·51587 at 79·1°; 4-*methyl*-2-*ethyl*, m. p. 67·5°, sp. gr. 1·0571, and n_a 1·51434 at 80·2°.

The preparation and constants of some ketones are also given: o-*methylacetophenone*, $CH_3{\cdot}CO{\cdot}C_6H_4Me$, from calcium *o*-toluate and calcium acetate, is a liquid boiling at 79°, 108°, and 214° under 5, 30, and 761 mm. pressure respectively; p-*methylacetophenone*, from toluene, acetyl chloride, and aluminium chloride, boils at 228° under 759 mm. pressure; m-*hydroxyacetophenone*, from *m*-nitroacetophenone, boils at 153° and 296° under 5 and 756 mm. pressure respectively, the *methyl*

ether boiling at 99°, 152°, and 252° under 4, 38, and 760 mm. pressure respectively; p-*hydroxyacetophenone*, from phenol, acetyl chloride, and zinc chloride, melts at 107°, the *methyl ether*, from anisole, acetyl chloride, and aluminium chloride, melting at 35°. The optical constants are given for the following.

o-Hydroxybenzaldehyde, sp. gr. 1·1589 and n_α 1·56422 at 21·3°; *p*-hydroxybenzaldehyde, sp. gr. 1·1291 and n_α 1·57055 at 130°; *o*-methylacetophenone, sp. gr. 1·0010 and n_α 1·52415 at 16·8°; *p*-methylaceto phenone, sp. gr. 1·0029 and n_α 1·52827 at 22°; *p*-tolyl pentadecyl ketone, sp. gr. 0·8665 and n_α 1·46954 at 77·3°; *p*-tolyl heptadecyl ketone, sp. gr. 0·8621 and n_α 1·46799 at 78°; *p*-anisyl pentadecyl ketone, sp. gr. 0·8981 and n_α 1·47605 at 80·5°; *o*-hydroxyacetophenone, sp. gr. 1·1302 and n_α 1·55405 at 18·2°; *o*-ethoxyacetophenone, sp. gr. 1·0036 and n_α 1·49684 at 78·3°; *m*-hydroxyacetophenone, sp. gr. 1·0992 and n_α 1·53482 at 109·2°; *m*-methoxyacetophenone, sp. gr. 1·0943 and n_α 1·53665 at 19°; *p*-hydroxyacetophenone, sp. gr. 1·1090 and n_α 1·55773 at 109·2°; *p*-methoxyacetophenone, sp. gr. 1·0493 and n_α 1·52395 at 79·9°; *p*-acetyl-*m*-hydroxytoluene, sp. gr. 1·0592 and n_α 1·53689 at 135·3°. G. D. L.

Quinonoid Derivatives of Diphenyl. II. RICHARD WILLSTÄTTER and LUDWIG KALB (*Ber.*, 1905, **38**, 1232—1241. Compare Abstr., 1904, i, 1050).—*Diphenoquinone*, $C_{12}H_8O_2$, prepared by shaking diphenol dissolved in ether with lead peroxide for a day and subsequently, after decanting the ether, boiling the residue with benzene for a short time, is obtained either in hard, glistening, blue or brownish-red needles or in soft golden-yellow to bronze, minute needles. The first form is converted into the second on adding a trace of diphenol to the hot saturated solution or by precipitating the benzene solution with light petroleum. On heating, it decomposes at about 165°.

Diphenoquinhydrone, $C_{24}H_{18}O_4$, is best prepared by mixing molecular quantities of diphenoquinone in benzene and diphenol dissolved in ether; it crystallises in dark green needles, which decompose at 180°, and forms a violet-coloured *sodium* salt.

By the oxidation of benzidine with lead peroxide, a compound, $C_{12}H_{10}N_2$, is obtained, probably the *di-imine* of diphenoquinone. This crystallises from benzene in well-formed, long, reddish-brown needles pointed at both ends, melts at 285—286°, and dissolves in concentrated sulphuric acid with a blood-orange-red coloration. E. F. A.

Disulphonic Acids of Anthraquinone. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 157123).—When the sulphonation of anthraquinone in the presence of a mercury salt (Abstr., 1904, i, 513) is carried out at a higher temperature or for a longer time, or if a larger quantity of sulphur trioxide is used, the product is a mixture of anthraquinone-1:5- and -1:8-disulphonic acids, which is readily separated into its components. Sulphonation in the β-position does not take place, as in the ordinary process of sulphonation of anthraquinone. C. H. D.

Nitro-derivatives of Alkylaminoanthraquinones. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 156759).—The secondary and tertiary alkyl derivatives of aminoanthraquinones and their

sulphonic acids (Abstr., 1903, i, 498, 839), unlike the parent amino-compounds, are readily nitrated by means of nitric and sulphuric acids. In the case of tertiary alkyl derivatives, one alkyl group is often eliminated, secondary alkyl derivatives being obtained. The nitro-group in the derivatives thus prepared is readily exchanged for arylamino-residues.

4-*Nitro*-1-*methylaminoanthraquinone*, prepared by nitrating α-methylaminoanthraquinone, crystallises from pyridine in long, glistening, reddish-brown needles and melts at 250°. It dissolves sparingly in alcohol or acetic acid, more readily in acetone, and is insoluble in dilute hydrochloric acid. 2-*Nitro*-1-*methylaminoanthraquinone* is formed at the same time, and may be separated by its greater solubility in organic solvents.

4 : 8-*Dinitro*-1 :5-*dimethylaminoanthraquinone* separates from pyridine in dark violet crystals and dissolves in pyridine to a bluish-red solution and in concentrated sulphuric acid to a yellow solution. The *nitrate* is colourless.

The colour-reactions of many similar derivatives are described.

C. H. D.

Methyl Ethers of Hydroxyanthraquinones. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 156762).—The α-sulphonic acids of anthraquinone react with methyl alcohol and sodium hydroxide on warming, the sulpho-group being replaced by the methoxy-group. Thus anthraquinone-α-sulphonic acid yields erythroxyanthraquinone methyl ether; anthraquinone-1 : 8-disulphonic acid yields chrysazin dimethyl ether, and anthraquinone-1 : 5-disulphonic acid yields anthrarufin dimethyl ether. C. H. D.

Action of Alcoholic Potassium Hydroxide on Phenanthraquinone. RICHARD MEYER and OSKAR SPENGLER (*Ber.*, 1905, **38**, 950—953).—The decomposition of the lactone, $C_{16}H_{10}O_4$, (this vol., i, 219), on melting is shown by an analysis of the gaseous products to take place quantitatively according to the equation $2C_{16}H_8O_3 = C_{29}H_{16}O_2 + CO_2 + 2CO$, the solid product being solely *didiphenylenepyrone*, $\begin{matrix} C_6H_4\cdot C\cdot CO\cdot C\cdot C_6H_4 \\ | \quad\;\; || \quad\quad\;\; || \quad | \\ C_6H_4\cdot C{-}O{-}C\cdot C_6H_4 \end{matrix}$, which is obtained colourless after repeated crystallisations. The formation of a six-membered ring from the coalescence of two five-membered rings is remarkable in view of Baeyer's tension theory. W. A. D.

Oxidation of *iso*Borneol to Camphor. CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERING (D.R.-P. 157590).—The yield of camphor obtained by oxidising *iso*borneol with potassium permanganate in acetic acid solution (Semmler, Abstr., 1900, i, 351) does not exceed ten per cent., but may be greatly increased by adding the *iso*borneol in powdered form, or dissolved in benzene or light petroleum, to an aqueous solution of permanganate, and agitating thoroughly.

C. H. D.

[Cinnamylidenecamphor and its Reduction Products.] HANS RUPE and GUNNAR FRISELL (*Ber.*, 1905, **38**, 1171).—A reply to Bruhl's

suggestion (this vol., i, 293) that inaccurate measurements of molecular refractions were made in a former paper (this vol., i, 220).

W. A. D.

Menthone derived from Hexahydrothymol. Léon Brunel (*Compt. rend.*, 1905, **140**, 792—794).—The two isomeric thymomenthols (hexahydrothymols; compare this vol., i, 197) obtained by direct reduction of thymol yield thymomenthone, $C_{10}H_{18}O$, when oxidised with chromic acid in acetic acid solution at about 0°.

Thymomenthone is a colourless, mobile liquid with an odour and taste resembling those of ordinary menthone. It boils at 212° under 760 mm., has a sp. gr. 0·911 at 0°, and does not crystallise when cooled to −10°. When reduced by sodium in alcoholic solution, or by hydrogen in presence of finely-divided nickel, it forms β-thymomenthol. *Thymomenthonesemicarbazone* forms colourless, odourless crystals melting at 159°. *Thymomenthoneoxime* forms small, colourless needles melting at 80°. When the oxime is reduced by sodium in alcoholic solution, *thymomenthylamine* is obtained as a colourless liquid with a disagreeable odour, which boils at 208° under 760 mm., absorbs carbon dioxide from the air, and forms well-defined salts with acids. The *picrate* forms yellow needles, which are only slightly soluble in water and alcohol, and melts at 168—169°.

H. M. D.

Coagulation and Solubility of Caoutchouc. Carl Otto Weber (*Chem. Centr.*, 1905, i, 886; from *Gummi-Zeit.*, **19**, 354—356. Compare Abstr., 1904, i, 331).—The product obtained from caoutchouc milk by purely mechanical means, such as by centrifugal separation, for example, is termed "coalesced" caoutchouc in order to distinguish it from coagulated caoutchouc. These products have different physical properties, and are probably different polymerides. Since the caoutchouc molecule contains at least two, and probably three, double bonds for each $C_{10}H_{16}$ group, polymerisation cannot have affected the number of these bonds. The solubility even of the best kinds of crude Para caoutchouc has been found to vary within very great limits, and the author's previous statement that highly polymerised caoutchouc is insoluble in ether applies only to the particular kind of caoutchouc examined (fine cut sheet). The variations of solubility are so great that it is impossible to regard any solvent as the best. The portion which is soluble in ether can be isolated from carefully selected crude materials in the form of a hydrocarbon, $C_{10}H_{16}$. Fractional separation by means of other solvents always yields products which contain oxygen, the percentage of this element increasing slowly from fraction to fraction. The quantity of oxygen contained in the insoluble substance is greater the less the proportion of this substance contained in the original material. Fendler's results (*Gummi-Zeit.*, **19**, 41) only show that the amount of insoluble substance varies within extremely wide limits. The quality of caoutchouc is, doubtless, to some extent dependent on the insoluble portion, for in the process of milling this substance practically disappears.

E. W. W.

Caoutchouc. Decomposition and Constitution of Para Caoutchouc. Carl D. Harries (*Ber.*, 1905, **38**, 1195—1203. Compare Abstr., 1904, i, 757).—A current of ozonised oxygen, containing 5·5—6 per cent. of ozone, was passed into a cooled solution of Para caoutchouc in chloroform, and when the product had been concentrated under diminished pressure, a mixture of ethyl acetate and light petroleum was added. *Caoutchouc ozonide*, $C_{10}H_{16}O_6$, separated as an oil, which solidified to a glassy mass and melted at about 50°; it is explosive. When water was added and the product then submitted to distillation in a current of steam, lævulic aldehyde passed over. The distillate reduced Fehling's solution, gave an intense pyrrole reaction, and with phenylhydrazine acetate formed phenylmethyldihydropyridazine, melting at 197° and identical with the product directly obtainable from lævulic aldehyde. The presence of the latter in the distillate was further proved by the formation of its dioxime, and by its isolation. Lævulic aldehyde has the sp. gr. 1·016 at 21·5° and n_D 1·42695 at 21·5°.

When the ozonide is distilled with steam until the distillate ceases to give the pyrrole reaction, the residue contains lævulic acid.

When the action of steam on the ozonide is carried out for a short time only, *lævulic aldehyde peroxide*, melting and decomposing at 197°, separates. It crystallises from water in leaflets and is readily converted by steam into lævulic aldehyde. It liberates iodine from potassium iodide, decolorises potassium permanganate and indigo solutions, reduces ammoniacal silver nitrate, and deflagrates when quickly heated.

No other volatile aldehydes or ketones result as products of the decomposition of the ozonide. The products obtained are readily estimated quantitatively.

The decomposition of the ozonide into lævulic aldehyde and its peroxide is represented as follows:

$$C_{10}H_{16}O_6 = CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CHO + \begin{array}{l} O{:}O{:}CH-CH_2 \\ \,|\;\;\;\;\;\;\;\;\;\;\;\;\;\;\;\;\;\;| \\ O{:}O{:}CMe\cdot CH_2 \end{array}.$$

Caoutchouc is a cyclic compound. The formula

$$\left[CMe{<}\begin{array}{l}CH_2\cdot CH_2\cdot CH\\CH\cdot CH_2\cdot CH_2\end{array}{>}CMe\right]_x$$

may provisionally be assigned to it. Caoutchouc is optically inactive.

A. McK.

Aucubin, the Glucoside of Aucuba Japonica. Émile Bourquelot and Henri Hérissey (*Ann. Chim. Phys.*, 1905, [viii], **4**, 289—318).—A *résumé* of work already published (compare Abstr., 1902, i, 634; ii, 55; 1904, i, 606). Crystalline hydrated aucubin has $[\alpha]_D$ −164·9°, whilst the anhydrous compound has $[\alpha]_D$ −174·4°.

M. A. W.

Digitonin. Heinrich Kiliani (*Arch. Pharm.*, 1905, **243**, 5—12).—A reply to Cloetta (*Arch. exp. Path. Pharm.*, 1901, **45**, 435; also 1898, **41**, 421). Cloetta's "amorphous digitonin" is certainly a mixture, and so simple a formula for it as $C_{28}H_{47}O_{14}$ is out of the question.

C. F. B.

Preparation of a Non-poisonous Saponin. FIRMA EMANUEL MERCK (D.R.-P. 156954).—The saponin extracted from the leaves, bark, and other portions of *Bulnesia Sarmienti* or *Guaiacum officinale* by means of benzene, and purified by means of lead acetate, is neutral and non-poisonous, and does not exert a solvent action on red blood-corpuscles. Its formula is $C_{22}H_{36}O_{10}$, and it appears to be a methyl derivative of saponic acid, $C_{21}H_{34}O_{10}$. It dissolves readily in water or alcohol, and is precipitated by ether as a dull yellow powder.

C. H. D.

Bilirubin, the Red Colouring Matter of the Bile. WILLIAM R. ORNDORFF and JOHN E. TEEPLE (*Amer. Chem. J.*, 1905, **32**, 215—250).—In a previous paper (Abstr., 1901, i, 602), it was shown that bilirubin does not contain alkoxyl-groups, but has one alkyl group attached to nitrogen, and is probably a pyrrole derivative; analysis showed that its composition could be expressed by the formula

$$C_{34}H_{36}O_7N_4.$$

Küster (Abstr., 1902, i, 388) has demonstrated that the material used in this investigation was a mixture of two substances which differ in composition and solubility in chloroform.

It is now found that pure crystalline bilirubin has the composition $(C_{16}H_{18}O_3N_2)_x$ and crystallises from chloroform in monoclinic or triclinic prisms; its solubility cannot be determined with accuracy on account of its tendency to form supersaturated solutions. On reduction with zinc dust or nascent hydrogen iodide, it is converted into hæmopyrrole.

By the action of tribromobenzenediazonium hydrogen sulphate on bilirubin, two compounds are produced, a *monoazo*-derivative,

$$C_{32}H_{35}O_6N_4{\cdot}N_2{\cdot}C_6H_2Br_3,$$

and a *bisazo*-derivative, $C_{32}H_{34}O_6N_4(N_2{\cdot}C_6H_2Br_3)_2$. These products are easily distinguishable, as the former gives a red and the latter a purple colour with potassium hydroxide. Determinations of the molecular weight of the bisazo-compound in chloroform or ethyl acetate solution by the ebullioscopic method confirm the above formula, whence it must be concluded that bilirubin has the formula

$$C_{32}H_{36}O_6N_4.$$

On repeating the work of Pröscher (Abstr., 1900, i, 571), it has been found that acetophenonediazonium chloride combines with bilirubin forming both *azo*- and *bisazo*-derivatives, which are best separated by means of carbon disulphide; the latter compound,

$$C_{32}H_{34}O_6N_4(N_2{\cdot}C_8H_7O)_2,$$

crystallises in long, wedge-shaped plates of the triclinic system and is identical with Pröscher's substance. The azo-compound,

$$C_{32}H_{35}O_6N_4{\cdot}N_2{\cdot}C_8H_7O,$$

is insoluble in carbon disulphide and only slightly soluble in chloroform. All these azo-derivatives of bilirubin show characteristic absorption bands which are fully described.

E. G.

Tannins producing a "Bloom" [on Leather]. M. NIERENSTEIN (*Chem. Centr.*, 1905, i, 701; from *Collegium*, 1905, 21—23).—Pyro-

gallol tannins give a "bloom" of ellagic acid on leather, the acid being formed either by synthesis from gallic esters or by decomposition of ellagic glucosides already existing in the tannin. Myrobalans yielded ellagic acid on extraction with hot water and crystallisation. *Tetra-acetylellagic acid*, $C_{22}H_{16}O_{12}$, melts at 276—279° and, on warming with concentrated sulphuric acid, gives colourless ellagic acid, which is not coloured by nitric acid. The original mother liquor, after warming with dilute sulphuric acid, yields gallic acid on extraction with ether and pyrogallol on subsequent extraction with ethyl acetate. Dextrose is present in the aqueous residue. G. D. L.

A Second Synthesis of Apigenin. MARIE BREGER and STANISLAUS VON KOSTANECKI (*Ber.*, 1905, **38**, 931—933).—5 : 7 : 4′-Trimethoxyflavanone (Kostanecki, Lampe, and Tambor, Abstr., 1904, i, 441) reacts with a chloroform solution of bromine yielding 3 : 6 : 8-*tribromo*-5 : 7 : 4′-*trimethoxyflavanone*, $C_6Br_2(OMe)_2<\begin{matrix}O—CH\cdot C_6H_4\cdot OMe\\ CO\cdot CHBr\end{matrix}$, which melts and decomposes at 145°. Alcoholic potash converts this into 6 : 8-*dibromo*-5 : 7 : 4′-*trimethoxyflavone*,

$$C_6Br_2(OMe)_2<\begin{matrix}O—C\cdot C_6H_4\cdot OMe\\ CO\cdot CBr\end{matrix},$$

which crystallises in needles melting at 245°. When boiled with concentrated hydriodic acid for several hours, it yields 5 : 7 : 4′-trihydroxyflavone (Czajkowski, Kostanecki, and Tambor, Abstr., 1900, i, 504). J. J. S.

3′-Hydroxyflavonol. A. GUTZEIT and STANISLAUS VON KOSTANECKI (*Ber.*, 1905, **38**, 933—935. Compare Kostanecki and Lampe, Abstr., 1904, i, 440; Kostanecki and Stoppani, *ibid.*, 443).—*o*-Hydroxyacetophenone condenses with *m*-methoxybenzaldehyde yielding 2′-*hydroxy*-3-*methoxychalkone*, $OH\cdot C_6H_4\cdot CO\cdot CH\colon CH\cdot C_6H_4\cdot OMe$, which crystallises from alcohol in yellow plates melting at 94—95° and soluble in concentrated sulphuric acid. When boiled with an aqueous alcoholic solution of sulphuric acid, it yields 3′-*methoxyflavanone*, which crystallises in colourless prisms melting at 77—78°. 3-iso*Nitroso*-3′-*methoxyflavanone*, $C_6H_4<\begin{matrix}O—CH\cdot C_6H_4\cdot OMe\\ CO\cdot C\colon N\cdot OH\end{matrix}$, crystallises from benzene in colourless needles, melts and decomposes at 159—160°, and when boiled with a mixture of acetic and 10 per cent. sulphuric acid yields 3′-*methoxyflavonol*, $C_6H_4<\begin{matrix}O—C\cdot C_6H_4\cdot OMe\\ CO\cdot C\cdot OH\end{matrix}$, which crystallises from alcohol in pale yellow plates melting at 134°. Its solution in concentrated sulphuric acid is pale greenish-yellow, and when warmed with sodium hydroxide it yields a sparingly soluble *sodium* derivative with an intense yellow colour. The *acetyl* derivative melts at 117—118°. The methoxy-compound when hydrolysed with concentrated hydriodic acid, yields 3′-*hydroxyflavonol*, $C_{15}H_{10}O_4$, in the form of pale yellow needles melting at 237°; the *acetyl* derivative melts at 166°. J. J. S.

An Isomeride of Quercitol. STANISLAUS VON KOSTANECKI and FR. RUDSE (*Ber.*, 1905, 38, 935—938).—Gallacetophenone dimethyl ether condenses with veratraldehyde yielding *2'-hydroxy-3' : 4' : 3 : 4-tetramethoxychalkone*, $OH\cdot C_6H_2(OMe)_2\cdot CO\cdot CH:CH\cdot C_6H_3(OMe)_2$, in the form of yellow needles melting at 124° and soluble in concentrated sulphuric acid to a reddish-yellow solution; the *acetyl* derivative melts at 119°. When boiled with alcohol and dilute hydrochloric acid, it yields *7 : 8 : 3' : 4'-tetramethoxyflavanone*, $C_{19}H_{20}O_6$, which crystallises from carbon disulphide in colourless, glistening needles melting at 144°. The iso*nitroso*-derivative forms pale yellow needles melting and decomposing at 172° and soluble in sodium hydroxide solution; when heated with acetic and dilute sulphuric acids, it yields *7 : 8 : 3 : 4-tetramethoxyflavonol*, $C_{19}H_{18}O_7$, in the form of pale yellow needles melting at 217°. The *acetyl* derivative melts at 176°.

Concentrated hydriodic acid hydrolyses the the tetramethyl ether to *7 : 8 : 3' : 4'-tetrahydroxyflavonol*, $C_{15}H_{10}O_7,H_2O$, a compound closely resembling fisetin. It melts and decomposes at 308° and is a good dye for mordanted fibres. It dissolves in dilute alkalis yielding reddish-yellow solutions and yields a *penta-acetyl* derivative melting at 172—173°.

J. J. S.

Influence of Light and Heat on the Chlorination and Bromination of Homologues of Thiophen. ST. OPOLSKI (*Bull. Acad. Sci. Cracow*, 1904, 727—732).—Chlorination and bromination of 2-methyl- or 2-ethyl-thiophen in sunlight results almost exclusively in the substitution of halogen in the ring, only very small quantities of halogen entering the side-chain. The bromination was effected by means of bromine vapour in a current of carbon dioxide, and in the case of 2-methylthiophen resulted in the formation of *bromo-2-methylthiophen*, which forms a liquid of pleasant odour, boiling at 177° (corr.) under 740 mm. pressure and having a sp. gr. 1·5529 at 20°/4° and n_D 1·5673. It gives an emerald-green coloration with phenanthraquinone and sulphuric acid in acetic acid solution, and an olive-violet indophenin reaction. The solid products of bromination are tribromo-2-methylthiophen and a *dibromo-2-methylthiophen*, which forms colourless needles, melts at 44—45°, and is readily soluble in warm alcohol or ether. When boiling 2-methylthiophen is brominated, the same products are formed, but there is considerable charring.

Under similar conditions, chlorination leads to the production mainly of *chloro-2-methylthiophen*, which boils at 153·7° (corr.) under 738 mm. pressure, has a sp. gr. 1·2016 at 17°/4°, n_D 1·5367, and gives a yellowish-green Laubenheimer reaction, the violet indophenin colour being produced with greater difficulty.

Bromination of 2-ethylthiophen leads to the formation of the known bromo-2-ethylthiophen, which boils at 90—100° under 30—40 mm. pressure, has a sp. gr. 1·4642 at 20°/4°, and n_D 1 5576 at 20°.

G. D. L.

Alkine Esters of Hydroxy-acids. CHININFABRIK BRAUNSCHWEIG; BUCHLER & Co. (D.R.-P. 157693).—It is not possible to condense fatty

hydroxyacyl chlorides with alkines, internal condensation taking place. Esters containing an acyloxy-group, however (Abstr., 1904, i, 685), react readily, and the acyl group may then be removed by hydrolysis with acids. The preparation of inactive atropine from acetyltropyltropeine, of tropyl-lupineine from acetyltropyl-lupineine, and of salicyltropeine from acetylsalicyltropine, is described. C. H. D.

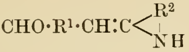
Alkaloid from Papaver Dubium. VITTORIO PAVESI (*Chem. Centr.*, 1905, i, 826—827; from *Rend. R. Ist. Lomb. sci. lett.*, [ii], **38**, 117—121).—By extraction of the seed capsules of *Papaver dubium* with light petroleum, a previously unknown alkaloid, *aporeine*, is obtained. The thick, yellow, amorphous extractive product, amounting to 0·015 per cent., yields with 10 per cent. hydrochloric acid the *hydrochloride*, which forms glistening scales melting at about 230°, and gives precipitates with silver nitrate and phosphomolybdic acid. The base forms microscopic leaflets after crystallisation from ether, light petroleum, or chloroform. When a solution of a trace of the alkaloid or its hydrochloride in a drop of nitric acid of sp. gr. 1·3 is dropped into concentrated sulphuric acid, a violet, brown, and finally yellow coloration is produced, a similar result being given by the base with strong sulphuric acid in which a crystal of potassium chlorate has been dissolved. The hydrochloride gives a greyish-blue, green, brown, and finally yellow coloration with Fröhde's reagent; a green, blue, and finally black coloration with a solution of 2 or 3 drops of 40 per cent. formalin in 3 c.c. of concentrated sulphuric acid; with strong sulphuric acid, especially in the presence of potassium nitrate, or with fuming nitric and sulphuric acids in the presence of potassium dichromate, a brown coloration.

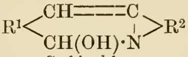
The hydrochloride produces on the tongue at first a burning and then a numbing sensation. The alkaloid is a tetanus poison similar to thebaine. G. D. L.

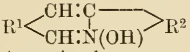
Constitution of ψ-Ammonium Bases with reference to the Alkaloids and the Products these yield by Transformation. JOHANNES GADAMER (*Arch. Pharm.*, 1905, **243**, 12—29. Compare Decker, Abstr., 1902, i, 691).—A theoretical paper introductory to those following it (see next abstract and this vol., i, p. 353). The author considers that the ψ-ammonium bases exhibit a peculiar kind of tautomerism, such as renders possible the existence of three isomerides, one of which, however, may sometimes be too unstable to form derivatives. The relationship between these tautomeric forms is indicated by the following atomic groupings: (1) ammonium base proper, ·NMe(OH):CH·; (2) carbinol base, ·NMe·CH(OH)·; (3) aldehyde (or ketone) base, ·NHMe with ·CHO. It will be seen that the formation of the last form involves the breaking of a bond within the formula of the molecule, and consequently a lessening of the number of rings present.

The triphenylmethane dyes form a special group of ψ-bases, in which the structure of the molecule excludes the possibility of an aldehydic (or ketonic) form existing. C. F. B.

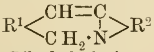
Berberine. JOHANNES GADAMER (*Arch. Pharm.*, 1905, **243**, 31—43). —Berberine, $C_{20}H_{19}O_5N$, may exist in three tautomeric forms (compare Abstr., 1902, i, 173; preceding abstract) [$R^1 = C_6H_2(OMe)_2$; $R^2 = C_6H_2(\colon O_2\colon CH_2)\cdot CH_2\cdot CH_2\cdot$]:


Aldehyde base.


Carbinol base.


Ammonium base proper.

The free base in the solid state probably has the aldehydic constitution; the ammonium base only exists in aqueous solution, and even then changes in time to the aldehydic form, the alkalinity of the solution gradually disappearing. Its transformation under the influence of alkali into a mixture of dihydroberberine and hydroxyberberine (Abstr., 1902, i, 555) is analogous to that of benzaldehyde into benzyl alcohol and benzoic acid, for the two substances,


Dihydroberberine.

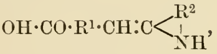
and


Oxyberberine.

may be regarded respectively as the anhydride of the


Primary alcohol.

and


Carboxylic acid.

corresponding with the aldehydic form of berberine. Further, an oxime was prepared, although with difficulty; berberine sulphate, mixed with a little water, was treated gradually with sodium hydroxide until it had dissolved as the soluble normal sulphate, excess of the alkali was added, and the precipitated alkaloid was shaken out with ether; to the (filtered) ethereal solution, a hydroxylamine solution was added that had been made by pounding together hydroxylamine hydrochloride and crystallised sodium carbonate, adding some alcohol, then adding a larger volume of ether, and filtering. Flakes first separated which melted at 188—191° and contained C 59·7, H 5·6, N 4·4; then the oxime crystallised out slowly in satisfactory yield; in one experiment, reddish-yellow needles melting and decomposing at 120—122° were obtained in addition. *Berberinaldoxime*, $C_{20}H_{20}O_5N_2$, decomposes at about 165° and is an unstable substance; hydrochloric acid does not form a salt with it, berberine chloride being obtained instead.

As the aldehydic formula contains a :NH group, it might be expected that free berberine (berberinaldehyde) would react with methyl iodide to form a quaternary iodide with the group $\colon NMe_2I$; also that it would form a benzoyl derivative with the group :NBz. Neither of these expectations could be realised, however; evidently the aldehydic form of berberine is not a very stable one. C. F. B.

Tarconine Methiodide and its Relations to Cotarnine and Hydrocotarnine. DANIEL BRUNS (*Arch. Pharm.*, 1905, **243**, 57—69).—Tarconine methiodide was prepared from narcotine by oxidation with iodine in alcoholic solution, and was reduced to hydrocotarnine with zinc and dilute sulphuric acid. This hydrocotarnine was identical with that obtained by reducing cotarnine, prepared from narcotine by oxidation with dilute nitric acid at 49°, with zinc and dilute sulphuric acid; in both cases, the hydrobromide was obtained anhydrous, contrary to what is often stated. Hydrocotarnine is oxidised by iodine in alcoholic solution at 100° completely to tarconine methiodide; four atoms of hydrogen are lost, just as is the case with tetrahydroberberine and corydaline. Alcoholic iodine in relatively smaller quantity oxidises hydrocotarnine to cotarnine, and cotarnine to tarconine methiodide, but in both cases the yield was far from quantitative. *Tarconine methyl hydrogen sulphate*, $C_{12}H_{11}O_3N,H_2SO_4$, was prepared in the crystalline state and analysed.

Methyltarconium hydroxide, the base corresponding with tarconine methiodide,

$$CH_2{<}\begin{matrix}OC{:}C(OMe){\cdot}C{\cdot}CH{:}NMe{\cdot}OH \\ OC{:}CH\text{——}C{\cdot}CH{:}CH\end{matrix} \left(= R''{<}\begin{matrix}CH{:}NMe{\cdot}OH \\ CH{:}CH\end{matrix}\right),$$

will not condense with hydroxylamine, nor could tarconine methiodide be made to yield definite products by reacting with acetone, chloroform, or ammonium sulphide even in the presence of an alkali. Evidently the base has little tendency to react in a tautomeric aldehydic form, $CHO{\cdot}R''{\cdot}CH{:}CH{\cdot}NHMe$ (compare this vol., i, 368).

Since tarconine methiodide is yellow whilst cotarnine iodide and hydrocotarnine are colourless, the chromophoric group must be the $\cdot CH{:}CH\cdot$ group, the carbon atoms of which are printed in thicker type in the formula of tarconine methiodide below:

$$R''{<}\begin{matrix}CH{:}NMeI \\ \mathbf{C}H{:}\mathbf{C}H\end{matrix} \qquad R''{<}\begin{matrix}CH{:}NMeI \\ CH_2{\cdot}CH_2\end{matrix} \qquad R''{<}\begin{matrix}CH_2{\cdot}NMe \\ CH_2{\cdot}CH_2\end{matrix}$$

Tarconine methiodide. Cotarnine iodide. Hydrocotarnine.

C. F. B.

Synthesis of Ephedrine. ERNST SCHMIDT [with F. FLAECHER] (*Arch. Pharm.*, 1905, **243**, 73—78).—Cinnamyl chloride,

$$CHPh{:}CH{\cdot}CH_2Cl,$$

unites with trimethylamine in alcoholic solution at the ordinary temperature to form *cinnamyltrimethylamine chloride*,

$$CHPh{:}CH{\cdot}CH_2{\cdot}NMe_3Cl,$$

which is left as a syrup when the alcohol is evaporated; the *aurichloride* and *platinichloride*, melting at 181° and 209·5—211·5° respectively, were analysed. The chloride in alcoholic solution unites with bromine to form the crystalline dibromide,

$$CHPhBr{\cdot}CHBr{\cdot}CH_2{\cdot}NMe_3Cl,$$

which melts at 141—142°. Boiled with water, this yields bromostyrene, trimethylamine, and a *bromohydrin*,

$$OH{\cdot}CHPh{\cdot}CHBr{\cdot}CH_2{\cdot}NMe_3Cl,$$

the *platinichloride* of which, less soluble than that of trimethylamine,

was analysed. When the bromohydrin is reduced with zinc and dilute sulphuric acid, there is formed, in addition to an oil much resembling the alcoholic substance, $C_9H_{10}O_3$, obtained by Miller (Abstr., 1903, i, 110) in the distillation of methylephedrine methohydroxide, the chloride of a *base*, $OH\cdot CHPh\cdot CH_2\cdot CH_2\cdot NMe_3Cl$, the *aurichloride* of which melts at 170°. These substances much resemble the isomeric derivatives of ephedrine and ψ-ephedrine, but are devoid of optical activity. When the free base is boiled in aqueous solution, an odour is perceptible resembling that of the oil mentioned above.

Cinnamylamine, $CHPh:CH\cdot CH_2\cdot NH_2$, contrary to what has been stated, can be obtained in good yield by allowing cinnamyl chloride to remain for 8 days at the ordinary temperature with ten times its weight of alcoholic ammonia. C. F. B.

Products formed under Various Conditions by the Action of Halogens on *d*-Lupanine. ARTURO SOLDAINI (*Chem. Centr.*, 1905, i, 826; from *Boll. Chim. Farm.*, **44**, 85—90. Compare Abstr., 1902, i, 392, 638).—From the product of the action of bromine on *d*-lupanine, a compound, $C_9H_{15}ON$, has been separated by means of its *platinichloride*, which melts and decomposes at about 200°; the platinichloride of the base $C_8H_{13}ON$, previously described, melts and decomposes at 201—202°. The compound $C_8H_{11}NHBr$, which is also formed, readily undergoes change on treatment with silver chloride and then with auric chloride, yielding a salt $(C_6H_7N)_2,HAuCl_4$. The salts $(C_8H_{13}N)_2,H_2PtCl_6$ and $C_{11}H_{16}O_2N_2,HBr$ were also prepared, all of which easily undergo change on heating or by the addition of salts.

Lupanine appears to be closely related to sparteine. G. D. L.

Nicotine Camphorate. A. GAWALOWSKI (*Chem. Centr.*, 1905, i, 820; from *Pharm. Post*, **38**, 109).—Nicotine camphorate, formed when nicotine and camphoric acid are heated together at 250°, dissolves in alcohol without subsequently darkening, and dissolves sparingly in water. No turbidity is produced by potassium hydroxide or sulphuric acid in the aqueous solution; light petroleum extracts camphoric or hydroxycamphoric (?) acid from the acid solution. The chief portion of the product, insoluble in water, is yellow and resinous, and dissolves readily in alcohol to a deep yellow solution miscible with water. From the dilute alcoholic solution, light petroleum extracts a yellow constituent; after acidification with sulphuric acid and renewed extraction with light petroleum, traces of a colourless substance are obtained. G. D. L.

Molybdenum Compound of Nicotine. EMIL MESZLÉNYI (*Landw. Versuchs-Stat.*, 1905, **61**, 321—349).—*Nicotine ammonium molybdate* (*dinicotine ammonium molybdo-tetra-anhydromolybdate*),

$$2(C_{10}H_{14}N_2,H_2MoO_4),(NH_4)_2MoO_4,4MoO_3,$$

is prepared by adding to 400 c.c. of a 20 per cent. solution of ammonium molybdate 320 c.c. of 10 per cent. acetic acid and 100 c.c. of a 10 per cent. solution of nicotine. The mixture is shaken several times in a tall cylinder, rapidly filtered, and washed successively with water, alcohol, and ether. It is then dried at 48—50°.

It is a white substance, insoluble in water, soluble in acids, and is decomposed by alkalis. When treated with metallic solutions, it yields the corresponding metallic molybdate. It is optically inactive and has a sp. gr. 2·5407. When oxidised in acid and in alkaline solutions, it yields nicotinic acid and dipyridine respectively. It is a strong poison. N. H. J. M.

Lactam Formation from γ-Lactones and the Stability of the Pyrrolidone Nucleus. OTTO KÜHLING and FRANZ FALK (*Ber.*, 1905, 38, 1215—1228).—1-p-*Tolyl-2-methylpyrrolidone-2-carboxylonitrile* is obtained as a yellow oil on condensing ethyl lævulate, hydrogen cyanide, and *p*-toluidine; the corresponding *amide* crystallises in white leaflets melting at 175°. 1-p-*Tolyl-2-methylpyrrolidone-2-carboxylic acid*, $CO_2H\cdot CMe<\substack{CH_2\cdot CH_2\\ N(C_7H_7)}>CO$, prepared by the action of ice-cold fuming hydrochloric acid on the nitrile, crystallises in colourless plates melting at 204°; the *silver* salt separates in crystalline plates, the *methyl* ester was obtained only as a yellow oil, the anilide crystallises in plates, the *thioamide* melts and decomposes at 207—208°, and the *amidoxime* forms glistening needles melting at 163·5°.

1-m-*Tolyl 2-methylpyrrolidone-2-carboxylic acid* crystallises in aggregates of needles melting at 136°, the *silver* salt forms plates, and the *methyl* ester rosettes of needles; the *amide* crystallises in thick prisms melting at 198°, the *nitrile* was obtained as a dark brown oil.

1-o-*Tolyl-2-methylpyrrolidone-2-carboxylic acid* crystallises in needles melting at 209·5°; the *amide* separates in column-like crystals which melt at 215·5°, the *nitrile* is a viscid, yellow oil.

1-*β-Naphthyl-2-methylpyrrolidone-2-carboxylic acid*,

$$CO_2H\cdot CMe<\substack{CH_2\cdot CH_2\\ N(C_{10}H_7)}>CO,$$

separates in colourless plates melting at 231°, the *zinc* salt crystallises in prisms, the *methyl* ester melts at 104—105°, the thioamide at 151°, the *amidoxime* at 176°; the *amide* melts at 223° and the *nitrile*, obtained by condensing ethyl lævulate with hydrogen cyanide and β-naphthylamine, melts at 78·5°.

1-*α-Naphthyl-2-methylpyrrolidone-2-carboxylic acid* crystallises in needles and melts at 255°, the glistening needles of the *amide* melt at 247·5—248°, the *nitrile* being obtained as a dark brown oil, whilst the *methyl* ester melts at 91°.

1-m-*Xylyl-2-methylpyrrolidone-2-carboxylic acid* crystallises in prisms in stellar aggregates melting at 169°, the *copper* salt forms green plates and the *methyl* ester long plates which sinter at 93° and melt at 97·5°. The *amide* crystallises in colourless needles aggregated in rosettes and melts at 196°; the *nitrile* is a light yellow oil.

1-p-*Xylyl-2-methylpyrrolidone-2-carboxylic acid* separates from a mixture of acetone and petroleum in glistening needles melting at 226°, the *amide* crystallises and melts at 211°; the *nitrile* is a yellow oil.

1-as-o-*Xylyl-2-methylpyrrolidone-2-carboxylic acid* crystallises in needles melting at 192°; the *methyl* ester and *nitrile* are oils, the colourless crystals of the *thioamide* melt at 220°, the *amidoxime* melts at 110°, and the *amide*, which crystallises in plates, melts at 206—207°.

1-vic.-o-*Xylyl-2-methylpyrrolidone-2-carboxylic acid* forms large needles in stellar aggregates melting at 186°, the *thioamide* melts at 217°, the *amidoxime* at 122°, and the amide at 203°. E. F. A.

Synthesis of 2:3:5-Trimethylpyrrole. G. Korschun (*Ber.*, 1905, **38**, 1125—1130. Compare Abstr., 1904, i, 615; Feist, Abstr., 1902, i, 488).—*Ethyl αβ-diacetylbutyrate*, CHMeAc·CHAc·CO_2Et, is formed by the action of methyl chloroethyl ketone on ethyl sodioacetoacetate in ethereal solution. It reacts with ammonia, slowly at the ordinary temperature, more quickly on warming, to form *ethyl* 2 : 3 : 5-*trimethylpyrrole*-4-*carboxylate*, $NH<\begin{matrix}CMe\dot{:}CMe \\ CMe\dot{:}\overset{|}{C}\cdot CO_2Et\end{matrix}$, which is also formed when a current of ammonia is passed through a mixture of ethyl acetoacetate and methyl chloroethyl ketone with aqueous ammonia, heated in a reflux apparatus. It crystallises in matted, white needles, melts at 101·5—102·5°, is only slightly soluble in water or petroleum, but easily so in the other ordinary solvents, is volatile in a current of steam, and gives the pinewood pyrrole reaction. When heated with alcoholic potassium hydroxide at 120—125° in a sealed tube for 50 hours, the ethyl ester is hydrolysed, and, the carboxylic acid being unstable at that temperature, the product obtained is 2 : 3 : 5-*trimethylpyrrole.* This is a colourless oil, which boils at 75—76° under 14—15 mm., or at 180° under 768 mm. pressure.

Methyl 2 : 3 : 5-*trimethylpyrrole*-4-*carboxylate*, $C_9H_{13}O_2N$, is formed when a current of ammonia is passed through a heated mixture of methyl acetoacetate, methyl chloroethyl ketone, and aqueous ammonia; it melts at 124·5—126°. But if methyl acetoacetate and methyl chloroethyl ketone are shaken with aqueous ammonia, the product obtained forms large crystals, melts at 82—84°, gives only a slight pinewood reaction, and consists of methyl β-aminocrotonate with traces of the pyrrole derivative. G. Y.

Pyridine Mercuri-iodides. Maurice François (*Compt. rend.*, 1905, **140**, 861—863).—Complex iodides containing mercury and pyridine are obtained when a solution of pyridine hydriodide acts on mercuric iodide, or when a solution of pyridine hydrochloride is added to an aqueous solution containing 100 grams of mercuric iodide and 75 grams of potassium iodide per litre. The compound $(C_5NH_5,HI)_2,HgI_2$ is formed when pyridine is dissolved in concentrated hydrochloric acid and the solution mixed with five times its volume of the mercuric iodide solution. It forms colourless plates melting at 159°. The compound

$$C_5NH_5,HI,HgI_2,$$

formed in similar circumstances when the proportion of pyridine is smaller, crystallises in pale yellow needles which melt at 151°. When a solution of pyridine hydriodide is warmed with a large excess of mercuric iodide, two other iodides are obtained, $(C_5NH_5,HI)_2,3HgI_2$, which forms yellow crystals melting at 101°, and $C_5NH_5,HI,2HgI_2$, which crystallises in golden-yellow plates melting at 121°. These complex iodides are all decomposed by water with precipitation of mercuric iodide. H. M. D.

Action of Formaldehyde on Pyridine. EMANUEL FORMÁNEK (*Ber.*, 1905, **38**, 944—945).—A condensation product, C_5H_5N,H_2CO, is formed when pyridine is heated for several hours on the water-bath with an excess of 40 per cent. formaldehyde. It crystallises from hot alcohol in rosettes of small needles, is readily decomposed into its components, and yields a *platinichloride* which is also readily decomposed. J. J. S.

Ammonium Compounds. XVIII. Formation and Decomposition of Quaternary Ammonium Compounds of the Inert Bases. HERMAN DECKER [with S. GADOMSKA, F. SANDBERG, and A. STAVROLOPOULOS] (*Ber.*, 1905, **38**, 1144—1155).—Many "inert" bases, such as the 8-nitroquinolines, which do not combine additively with methyl iodide, readily interact with methyl sulphate; from the additive compound formed, the methiodide of the base may be obtained by the action of potassium iodide. Such methiodides are on warming rapidly decomposed quantitatively into methyl iodide and the base; they may be analysed by absorbing the methyl iodide with alcoholic silver nitrate. Methyl sulphate may in many instances profitably replace methyl iodide as a methylating agent, owing to its entering into action at 100°; the substances may be heated together in an open vessel, but moisture should be excluded as much as possible.

8-*Nitro*-1-*methylquinolinium* 1-*methosulphate*, forms white, deliquescent crystals, is very soluble in water, and with sodium picrate gives the *picrate*, $C_{16}H_{11}O_9N_5$, crystallising in yellow needles and melting at 176°; with sodium dichromate, it gives an analogous *dichromate* and with potassium iodide 8-*nitroquinoline methiodide* is obtained. This crystallises in blue cubes and decomposes when slowly heated at about 120°.

8-*Nitroquinoline ethiodide* forms orange-red crystals. On oxidising 8-nitro-1-methylquinolinium 1-ethosulphate with an alkaline solution of potassium ferricyanide, 8-*nitro*-1-*ethyl*-2-*quinolone* is obtained, which crystallises from methyl alcohol in sheaf-like aggregates and melts at 96°. The substance previously described (Decker and Stavrolopoulos, Abstr., 1903, i, 719) as 8-nitro-1-ethyl-2-quinolone, melting at 87° and obtained by the action of ethyl iodide on the sodium derivative of nitrocarbostyril, is really the *ethyl ether*, $NO_2\cdot C_9NH_5\cdot OEt$, of 8-nitrocarbostyril. Similarly, the 8-nitro-1-methyl-2-quinolone (Abstr., 1901, i, 654) melting at 125° is 8-nitrocarbostyril methyl ether.

6 : 8-*Dinitroquinoline methiodide* crystallises in needles, decomposes at 172°, and on careful oxidation gives 6 : 8-*dinitro*-1-*methyl*-2-*quinolone* melting at 185°.

3-*Bromo*-8-*nitroquinoline methiodide* decomposes at about 145°; 3-*bromo* 8-*nitro*-1-*methyl*-2-*quinolone* crystallises from alcohol in yellow needles and melts at 185—186°.

6 : 8-*Dibromoquinoline methiodide* decomposes at 178°; 6 : 8-*dibromo*-1-*methyl*-2-*quinolone* crystallises from methyl alcohol in white needles, melts at 125°, and is converted by phosphorus pentabromide into 2 : 6 : 8-*tribromoquinoline*, which crystallises in needles and melts at 165°. When the latter is heated with hydrochloric acid, 6 : 8-*dibromocarbostyril*, melting at 230°, is obtained.

5-*Nitro*-1 : 8-*dimethyl*-2-*quinolone*, prepared from 5-nitro-8-methylquinoline, crystallises in yellow needles and melts at 139°.

5 : 8-*Dibromoquinoline methiodide* crystallises in red needles and decomposes at 166°.

By means of methyl sulphate, 5-nitroquinoline can readily be separated from 8-nitroquinoline; at 80° only the 5-nitroquinoline gives rise to a quaternary salt, the 8-isomeride remaining unaffected.

Phenylacridine methiodide begins to decompose at 220—222°. *Phenylacridine ethiodide* decomposes at 215°. W. A. D.

6-Hydroxyquinolones and some Alkyl Haloid Derivatives of 5-Bromo-6-hydroxyquinoline. JOH. HOWITZ and M. BÄRLOCHER (*Ber.*, 1905, **38**, 887—892. Compare Abstr., 1903, i, 279).—5-*Chloro*-6-*hydroxy*-1-*ethylquinolone*, $\begin{array}{l}\mathrm{CH{:}CH{\cdot}C{\cdot}NEt{\cdot}CO} \\ \mathrm{OH{\cdot}C{=}CCl{\cdot}C{-}{-}CH{:}CH}\end{array}$, formed when 5-bromo-6-ethoxy-1-ethylquinolone is heated with concentrated hydrochloric acid in a sealed tube at 160—170°, crystallises in slender, white needles or prisms and melts at 210—212°. Similarly, 5-chloro-6-hydroxyquinoline is formed when 5-bromo-6-ethoxyquinoline is heated with concentrated hydrochloric acid.

5-*Bromo*-6-*hydroxy*-1-*methylquinolone* is formed by heating the corresponding methoxy-compound with hydrobromic acid at 130—140°; it crystallises in slender, yellow needles or prisms, melts at 271°, and forms an insoluble, crystalline *sodium* derivative.

5-*Bromo*-6-*hydroxyquinoline methiodide*, formed by heating the quinoline with methyl iodide at 90—100°, crystallises in yellow needles and melts and decomposes at 156—158°. The *methochloride*, $C_{10}H_9ONClBr,2H_2O$, formed by treating the methiodide with silver chloride, crystallises in slender, yellow needles and melts at 212—215°; the *platinichloride*, $(C_{10}H_9ONClBr)_2,PtCl_4,3H_2O$, crystallises in glistening, red prisms and melts at 270°; the *ammonium base*, $C_9H_6BrO{\cdot}NMe{\cdot}OH$, formed by the action of potassium hydroxide or moist silver oxide on the methochloride, separates from water in slender, glistening, red crystals and melts and decomposes at 218°. The *ethobromide*, $C_{11}H_{11}ONBr_2$, crystallises in colourless, glistening, short prisms, melts at 235°, and when treated with potassium hydroxide or moist silver oxide yields the *base*

$$C_{11}H_{12}O_2NBr,2H_2O,$$

which crystallises in glistening, red prisms and melts and decomposes at 204—206°. The benzylochloride of 5-bromo-6-hydroxyquinoline, $C_{16}H_{13}ONClBr,H_2O$, crystallises in small, yellow prisms and melts at 100—105°, or, when anhydrous, at 139—140°; the *platinichloride*, $(C_{16}H_{13}ONClBr)_2PtCl_4,3H_2O$, crystallises in slender, red prisms and melts at 198°; the *base*, $OH{\cdot}C_9H_5BrO{\cdot}N(C_7H_7){\cdot}OH,H_2O$, crystallises in slender, carmine needles or leaflets and melts and decomposes at 112°. G. Y.

Action of Phenylhydrazine on Alkyl Bromides and Iodides. JULES ALLAIN-LE CANU (*Bull. Soc. chim.*, 1905, [iii], **33**, 327—335. Compare Abstr., 1903, i, 778).—*Phenyldipropylhydrazine bromide*,

$N_2H_2Pr^{\alpha}_2PhI$, obtained by the general method (*loc. cit.*), forms faintly yellow, triclinic crystals [$a:b:c = 0.7029:1:0.5594$; $\alpha = 89°17'$, $\beta = 86°37'$, $\gamma = 93°48'$], melts at 85°, and is readily soluble in alcohol, somewhat less so in water. *Phenyldibutylhydrazine bromide* forms slightly yellow, triclinic crystals [$a:b:c = 0.7731:1:0.5273$; $\alpha = 89°56'$, $\beta = 89°58'$, $\gamma = 98°29'$], melts at 148°, and is fairly soluble in alcohol, less so in water. *Phenyldibutylhydrazine iodide*, $N_2H_2(C_4H_9)_2PhI$, forms colourless, triclinic crystals [$a:b:c = 2.3244:1:1.91$; $\alpha = 91°0'$, $\beta = 87°37'$, $\gamma = 101°43'$], melts at 95°, is moderately soluble in alcohol, and less so in water. Phenyldimethylhydrazine iodide, $N_2H_2Me_2 \cdot PhI$ (Genvresse and Bourcet, Abstr., 1899, i, 502), forms monoclinic crystals [$a:b:c = 1.8917:1:1.3967$; $\beta = 91°10'$]. The crystallographic measurements recorded were made by de Schulten.

The iodides of phenyl*iso*propylhydrazine and phenyldi*iso*butylhydrazine and the bromide of phenyldi*iso*amylhydrazine could not be prepared by the general method. T. A. H.

Conversion of Schiff's Bases into Hydrazones, Semicarbazones, and Oximes. HANS OTT (*Monatsh.*, 1905, 26, 335—348. Compare Ofner, Abstr., 1904, i, 818; Ullmann and Frey, Abstr., i, 423).—With phenylhydrazine, *p*-bromophenylhydrazine, *as*-phenylmethylhydrazine, *as*-phenylethylhydrazine, *as*-diphenylhydrazine, *as*-benzoylphenylhydrazine, semicarbazide, or hydroxylamine in alcoholic solution, the following Schiff's bases are converted into the corresponding hydrazones, semicarbazones, or oximes: benzylideneaniline, *m*-nitrobenzylideneaniline, *p*-methoxybenzylideneaniline, *p*-hydroxy-*m*-methoxybenzylideneaniline, piperonylideneaniline, anilino-opianic acid, benzophenoneanilide, benzylidene-*m*-nitraniline, benzylidene-*o*-toluidine, benzylidene-*m*-xylidine, benzylidene-β-naphthylamine. Anilpyruvic acid does not enter into the reaction. *as*-Diphenylhydrazine, semicarbazide, and hydroxylamine are used in the form of their hydrochlorides in presence of sodium acetate.

The following new substances are described: m-*nitrobenzylidene*-p-*bromophenylhydrazone* crystallises in red needles and melts at 150—152°. p-*Methoxybenzylideneaniline* melts at 60—62°. p-*Methoxybenzylidene*-p-*bromophenylhydrazone* crystallises in brown leaflets and melts at 146—147°. p-*Methoxybenzylidene*-as-*phenylmethylhydrazone* crystallises in white needles and melts at 110—112°. p-*Hydroxy*-m-*methoxybenzylideneaniline* crystallises in yellow needles and melts at 152—153°. p-*Hydroxy*-m-*methoxybenzylidenephenylmethylhydrazone* crystallises in white needles and melts at 116°. p-*Hydroxy*-m-*methoxybenzylidenephenylethylhydrazone* forms yellow crystals and melts at 83—86°. p-*Hydroxy*-m-*methoxybenzylidenediphenylhydrazone* crystallises in hexagonal leaflets and melts at 125—127°. p-*Hydroxy*-m-*methoxybenzylidenephenylbenzylhydrazone* forms white crystals and melts at 172—173°. p-*Hydroxy*-m-*methoxybenzylidenebenzoylphenylhydrazone* crystallises in white needles and melts at 171—173°. p-*Hydroxy*-m-*methoxybenzylidenesemicarbazone* melts at 229°. *Piperonylidenephenylbenzylhydrazone* forms white needles and melts at 127—130°. *Piperonylidenesemicarbazone* crystallises in white leaflets and melts at 230—233°. G. Y.

Mutual Replacement of Sugar Residues in Hydrazones. Emil Votoček and Rudolf Vondráček (*Ber.*, 1905, **38**, 1093—1095. Compare Abstr., 1904, i, 1055).—In aqueous or aqueous alcoholic solution, galactosephenylhydrazone and mannose form mannosephenylhydrazone and galactose; similarly, dextrosephenylmethylhydrazone and galactose form galactosephenylmethylhydrazone and dextrose. Dextrosediphenylhydrazone and arabinose react, when warmed with acetic acid in aqueous-alcoholic solution, to form arabinosediphenylhydrazone and dextrose. In aqueous solution, galactosephenylhydrazone and dextrosephenylmethylhydrazone form galactosephenylmethylhydrazone and dextrosephenylhydrazone. Those reactions which take place in neutral solution are accelerated by addition of acetic acid; in each case, a less soluble hydrazone is formed. G. Y.

3-Pyrazolones. August Michaelis (*Annalen*, 1905, **338**, 267—321. Compare Abstr., 1903, i, 288; 1904, i, 124, 624; and *Ber.*, 1059, **38**, 154).—1-Phenyl-5-methyl-3-pyrazolone, $NPh<\begin{matrix}NH-CO\\ CMe:CH\end{matrix}$, which hitherto has only been prepared with difficulty, can now be readily obtained by the action of phosphorus pentachloride on a mixture of acylphenylhydrazine and ethyl acetoacetate. It has both acid and basic properties, and with phosphorus oxychloride yields 3-chloro-1-phenyl-5-methylpyrazole, $NPh<\begin{matrix}N = CCl\\ CMe:CH\end{matrix}$, and with acid chlorides, benzoyl chloride, and benzenesulphonic chloride, derivatives which are either amides, $NPh<\begin{matrix}NBz\cdot CO\\ CMe:CH\end{matrix}$, or esters, $NPh<\begin{matrix}N = C\cdot OBz\\ CMe:CH\end{matrix}$. A methyl ether is formed by the action of methyl iodide and alkali hydroxide. Benzaldehyde (1 mol.) condenses with two mols. of the pyrazolone. The hydrogen atom in position 4 is readily replaced by halogens, and sodium nitrite and acetic acid convert the pyrazolones into green nitroso-derivatives. When heat d with methyl iodide, a methiodide, 3-antipyrine, is obtained. Benzenediazonium chloride reacts with 3-pyrazolone, giving 4-azobenzene derivatives (see this vol., i, 392). 3-Pyrazolone differs from 5-pyrazolone in not giving the pyrazole-blue reaction.

[With Carl Meyer.]—1-*Phenyl*-5-*methyl*-3-*pyrazolone* is prepared by adding phosphorus pentachloride slowly to a mixture of acetylphenylhydrazine and ethyl acetoacetate and finally heating to 100°; the mixture is then poured into water, ammonia added, and lastly the solution made exactly neutral with hydrochloric acid; it crystallises in needles melting at 166° and boiling at 344—345° (corr.), and exists also in a labile form melting at 157°. The *hydrochloride* crystallises (with $2H_2O$) in needles melting at 129°; the *sulphate*, which also crystallises in needles, is anhydrous and melts at 84°. The *picrate* crystallises in yellow plates melting at 141°. The *benzoyl* derivative, prepared by shaking an alkaline solution of the pyrazolone with benzoyl chloride, crystallises in needles melting at 64—65°, and the corresponding *benzenesulphonate* in needles melting at 76°. 4-*Chloro*-1-*phenyl*-5-*methyl*-

3-*pyrazolone*, $\mathrm{NPh}<\begin{array}{l}\mathrm{NH-CO}\\ \mathrm{CMe{:}CCl}\end{array}$, prepared by passing chlorine into a chloroform solution of the pyrazolone or by heating the pyrazolone with phosphorus pentachloride at 150°, forms prisms melting at 261°; the corresponding *bromo*-derivative forms leaflets melting and decomposing at 241°. The *benzylidene* derivative, $\mathrm{CHPh}\left[\mathrm{OC}<\begin{array}{l}\mathrm{CMe\cdot NPh}\\ \mathrm{CO-NH}\end{array}\right]_2$, prepared by heating the pyrazolone with benzaldehyde at 100°, is a white powder melting at 270°; the *compound* with anisaldehyde melts at 287°. 3-*Methoxy*-1-*phenyl*-5-*methylpyrazole* (*ψ*-3-*antipyrine*), $\mathrm{NPh}<\begin{array}{l}\mathrm{N{=\!=}C\cdot OMe}\\ \mathrm{CMe{:}CH}\end{array}$, is formed together with 3-antipyrine when a mixture of sodium ethoxide and the pyrazolone are treated with methyl iodide, and is a colourless oil boiling at 150—160° under 16 mm. and at 273—275° under the ordinary pressure. When heated with methyl iodide, the *ψ-methiodide* of 3-antipyrine,

$$\mathrm{NPh}<\begin{array}{l}\mathrm{N(MeI){:}C\cdot OMe}\\ \mathrm{CMe{=\!=}CH}\end{array},$$

is formed as colourless needles melting at 198°. The 3-*antipyrine* (1-*phenyl*-2 : 5-*dimethyl*-2 : 3-*oxypyrazole*), $\mathrm{CMe}<\begin{array}{l}\mathrm{CH-C-}\\ \mathrm{NPh\cdot NMe}\end{array}>\mathrm{O}$, is identical with Lederer's *iso*antipyrine (*J. pr. Chem.*, 1892, [ii], **45**, 40).

3-*Chloro*-1-*phenyl*-5-*methylpyrazole*, prepared by heating the pyrazolone with phosphorus oxychloride at 210°, is a viscid, colourless liquid, not solidifying at −10°, and boiling at 170° under 15 mm. and at 304° under the ordinary pressure, and having a sp. gr. 1·2054 at 19° and n_D 1·5845. The 3 : 5-*dichloro*-compound, $\mathrm{NPh}<\begin{array}{l}\mathrm{N{=\!=}CCl}\\ \mathrm{CMe{:}CCl}\end{array}$, prepared by heating the pyrazolone at 200° with phosphorus pentachloride, is a liquid. 3-*Chloro*-4-*bromo*-1-*phenyl*-5-*methylpyrazole*, prepared from 3-chloro-compound, is a yellowish-green oil boiling at 194° under 15 mm. pressure.

The *methiodide* of 3-chloro-1-phenyl-5-methylpyrazole crystallises in needles decomposing at 177°; the *methobromide* crystallises in needles melting at 197°. The *methochloride* (3-antipyrine chloride),

$$\mathrm{NPh}<\begin{array}{l}\mathrm{NMeCl{:}CCl}\\ \mathrm{CMe=CH}\end{array},$$

prepared from the methiodide and silver chloride or from 3-antipyrine and phosphorus oxychloride, crystallises in needles with H_2O melting and decomposing at 100°; its aqueous solution has a bitter taste and gives precipitates with potassium ferro- and ferri-cyanides, with phosphotungstic acid, bromine water, hydrogen platinichloride, hydrogen aurichloride, and picric acid. The *platinichloride* crystallises in red leaflets melting at 218°.

[With Wilhelm Hahn.]—2 : 3-*Thio*-1-*phenyl*-2 : 5-*dimethylpyrazole* (3-*thiopyrine*), $\mathrm{CMe}<\begin{array}{l}\mathrm{CH-C-}\\ \mathrm{NPh\cdot NMe}\end{array}>\mathrm{S}$, is obtained when potassium hydrosulphide and the methiodide of 3-chloro-1-phenyl-5-methylpyrazole are

mixed in concentrated solution, and forms colourless crystals melting at 136°; when distilled, it passes into a ψ-compound; its aqueous solution gives precipitates with bromine water, mercuric chloride, potassium ferro- and ferri-cyanides, hydrogen platinichloride and aurichloride, picric and sulphurous acids. The *hydriodide* crystallises in needles melting at 176°. The *methiodide* forms white crystals melting at 168°, the *methochloride* hygroscopic prisms melting at 184°, the *platinichloride* yellowish-red needles melting and decomposing at 205°, the *ethiodide* needles melting at 121°, the iso*propiodide* (with $2H_2O$) crystals melting at 99°, the *benzyl-iodide* needles melting at 146°, the *benzoyl-chloride* unstable crystals melting at 83°, and the *benzoyl-iodide* needles melting at 163°.

2 : 3-*Trioxythio*-1-*phenyl*-2 : 5-*dimethylpyrazole* (3-*thiopyrinetrioxide*), $CMe\!\left<\begin{array}{l}CH-C——SO_2\\NPh\cdot NMe\cdot O\end{array}\right.$, prepared by passing chlorine into an aqueous solution of 3-thiopyrine, or by treating with sodium sulphite the methiodide of 3-chloro-1-phenyl-5-methylpyrazole, crystallises in prisms melting at 285°.

3-*Thiomethyl*-1-*phenyl*-5-*methylpyrazole* (ψ-*thiopyrine*),

$$NPh\!\left<\begin{array}{l}N=C\cdot SMe\\CMe\!:\!CH\end{array}\right.,$$

prepared by dry distillation of thiopyrine or its methiodide under reduced pressure, forms a colourless liquid boiling at 175° under 10 mm., at 194° under 22 mm., and at 357° under the ordinary pressure. Its *hydrochloride* crystallises in needles melting at 132°, its *platinichloride* with $2H_2O$ in yellow needles melting and decomposing at 130°; the *methiodide* is identical with that from 3-thiopyrine, and the *ethiodide* forms prisms melting at 148°.

3-*Methylsulphone*-1-*phenyl*-5-*methylpyrazole*, $NPh\!\left<\begin{array}{l}N=C\cdot SO_2Me\\CMe\!:\!CH\end{array}\right.$, prepared by oxidation of ψ-thiopyrine with permanganate, crystallises in needles melting at 105°. 4-*Bromo*-3-*thiomethyl*-1-*phenyl*-5-*methylpyrazole* (*bromo*-3-ψ-*thiopyrine*), prepared from bromine and ψ-thiopyrine in chloroform solution, crystallises in colourless needles melting at 107°.

2 : 3-*Seleno*-1-*phenyl*-2 : 5-*dimethylpyrazole* (3-*selenopyrine*),

$$CMe\!\left<\begin{array}{l}CH-C——\\NPh\cdot NMe\end{array}\right>Se,$$

is prepared from potassium hydroselenide and 3-antipyrine chloride or the methiodide of 1-phenyl-5-methyl-3-pyrazolone, crystallises in yellow leaflets melting at 168°, and gives precipitates with the same reagents as the analogous sulphur compound. The *platinichloride* is a reddish-brown powder. The crystalline *mercurichloride* melts at 198°. The *hydriodide* forms unstable, yellow needles melting at 183°, the *methiodide* prisms melting at 80°, and the *ethiodide* needles melting at 132°. The selenopyrine forms, with bromine, a *tetrabromide* as red crystals melting at 69°, becoming a *dibromide* on heating; the latter crystallises in golden-yellow needles melting at 174°, and when heated with aqueous sodium carbonate yields the *methobromide* of 1-phenyl-5-methylpyrazole.

3-*Selenomethyl*-1-*phenyl*-5-*methylpyrazole* (3-ψ-*selenopyrine*),

$$NPh\Big\langle\begin{matrix} N = C{\cdot}SeMe \\ CMe{:}CH \end{matrix},$$

prepared by distilling the methiodide of 3-selenopyrine under reduced pressure, is a colourless liquid of unpleasant smell, boiling at 195° under 13 mm. pressure; its *hydrochloride* is a crystalline solid melting at 135°, and its *platinichloride*, crystallising with $2H_2O$, sinters at high temperatures; the *methiodide* is identical with that of 3-selenopyrine, and the *ethiodide* crystallises in needles melting at 110°. 3-ψ-*Selenopyrine tetrabromide*, $C_{11}H_{12}N_2Br_4Se$, is a yellowish-brown powder melting at 191°, and is converted by heating into the *bromide* of 3-ψ-selenopyrine, $C_{11}H_{11}N_2BrSe$, crystallising in white needles melting at 178°.

[With Johann Behrens.]—The *tolylmethylpyrazolones* are prepared from acetyltolylhydrazines and ethyl acetoacetate. 1-p-*Tolyl*-5-*methyl*-3-*pyrazolone*, $C_7H_7{\cdot}N\Big\langle\begin{matrix} NH-CO \\ CMe{:}CH \end{matrix}$, crystallises in needles melting at 196°, and the ortho-*derivative* in prisms melting at 169°. The *hydrochloride* of the *para*-compound crystallises in plates melting at 206°, and that of the ortho-*compound* in prisms melting at 190°; the *nitrates* were both prepared. The *benzoyl* derivative of the *para*-compound crystallises in needles melting at 47°, and that of the ortho-*compound* in prisms melting at 72°. The benzenesulphonic derivative of the para-*compound* crystallises in needles melting at 55°, and that of the ortho-*compound* at 80°. The *benzylidene* derivative of the para-*compound* is a crystalline powder melting at 278°; the derivatives of anisaldehyde are powders, the para-*derivative* melting at 270°, and the *ortho*- at 295°. 3-*Chloro*-1-*tolyl*-5-*methylpyrazoles* are prepared from the pyrazolone and phosphorus oxychloride; the para-*compound* is crystalline and melts at 49°, and boils at 176° under 15 mm. pressure, whilst the ortho-*compound* is an oil boiling at 162° under 15 mm. pressure. The *methiodide* of the *para*-tolylchloropyrazolone forms crystals melting at 202°, and that of the ortho-*derivative* crystals melting at 179°. 3-p-*Tolylpyrine*, $CMe\Big\langle\begin{matrix} CH \text{———} C \text{—} \\ N(C_7H_7){\cdot}NMe \end{matrix}\Big\rangle O$, crystallises in prisms melting at 98—100° and gives in aqueous solution with ferric chloride a dark red coloration; the ortho-*derivative* crystallises in needles melting at 97°; the *hydrochlorides* crystallise with H_2O, the *para*-compound melting at 133° and the ortho- at 186°. The *picrate* of the *p*-tolyl compound crystallises in yellow leaflets melting at 181°, and of the *o*-tolyl compound in yellow needles melting at 165°.

3-p-*Tolylthiopyrine* crystallises in leaflets melting at 223°, the ortho-*compound* in leaflets melting at 133°; they both yield yellow, crystalline precipitates with sulphur dioxide, that from the ortho-*derivative* alone being stable, and melting at 112°. The *methiodide* forms crystals melting at 168°, and that of the ortho-*compound* at 173°. *Thiotolylpyrinetrioxides*, $C_{12}H_{14}O_3N_2S$, are prepared from the methiodide and sodium sulphite, the para-*compound* melting at 281° and the ortho-*compound* at 278°. 3-ψ-*Thiotolylpyrines* (3-*thiomethyl*-1-*tolyl*-5-*methylpyrazoles*), $C_{12}H_{14}N_2S$, are prepared by distilling the methiodide under reduced pressure, the para-*compound* is an oil boiling at 151° under 31 mm., and the ortho-*com-*

pound an oil boiling at 135° under 32 mm. pressure. When oxidised with permanganate, they yield the *sulphones*; both crystallise in needles, the para-*compound* melting at 85° and the ortho-*compound* at 122°. K. J. P. O.

4-Nitro-5-pyrazolone. HENRY B. HILL and OTIS F. BLACK (*Amer. Chem. J.*, 1905, **33**, 292—300).—It has been shown by Hill and Hale (Abstr., 1903, i, 401) that by the action of sodium hydroxide on nitromalonic diacetyldialdoxime a substance is produced which is isomeric with fulminuric acid. It is now found that it is 4-*nitro-5-pyrazolone*, $\begin{matrix}CH{=}N\\ | \\ NO_2\cdot CH\cdot CO\end{matrix}\!\!>\!NH$; it forms small, colourless crystals, melts at 136—137°, and is soluble in water, alcohol, or ether, but less so in benzene, chloroform, or light petroleum; its *sodium*, *silver*, *barium*, and *lead* derivatives are described. On heating 4-nitro-5-pyrazolone with excess of phosphorus oxychloride in a sealed tube at 100°, 5-chloro-4-nitropyrazole (Meder, *Inaug. Diss.*, 1901) is obtained, which crystallises in white, slender needles, melts at 186—187°, and is freely soluble in alcohol, acetone, or hot water, and slightly so in ether, chloroform, or cold water.

By the action of bromine on the sodium derivative of 4-nitro-5-pyrazolone, *tribromopyrazole*, $NH\!<\!\begin{matrix}N{=}CBr\\ \quad | \\ CBr{:}CBr\end{matrix}$, is produced, which forms white, silky needles, sublimes at about 120°, melts at 181°, is volatile with steam, and is soluble in alcohol or ether; its *acetyl* derivative crystallises in white needles and melts at 105—106°; the *silver* derivative is also described.

When tribromopyrazole is prepared by the action of bromine vapour on sodium 4-nitro-5-pyrazolone, a small quantity of another *substance* is simultaneously produced, which crystallises in white needles, melts at 163—164°, yields an acetyl derivative, and is probably dibromonitropyrazole; it combines with bromine to produce an additive *compound* which forms orange-coloured crystals, and is insoluble in cold water, but is decomposed by boiling water with evolution of bromine and formation of the white compound melting at 163—164°. E. G.

Transformation of Dextrose into Methyliminazole. ADOLF WINDAUS and FRANZ KNOOP (*Ber.*, 1905, **38**, 1166—1170).—On leaving dextrose at the ordinary temperature with zinc hydroxide dissolved in ammonia, it gives rise to 10 per cent. of its weight of pure 4-(or 5-)methyliminazole [4-(or 5-)methylglyoxaline], $\begin{matrix}CMe\cdot NH\\ \| \\ CH{-\!\!-}N\end{matrix}\!\!>\!CH$, identical with Gabriel and Pinkus' base (Abstr., 1893, i, 734; compare Jowett and Potter, Trans., 1903, **83**, 464). This substance, when subjected to the Schotten-Baumann method of benzoylation, gives rise to *dibenzoylpropylenediamine*,

$$NHBz\cdot CMe{:}CH\cdot NHBz,$$

which crystallises from alcohol in long needles and melts at 142°. 4-(or 5-)*Methylglyoxaline oxalate* crystallises from acetone and melts

and decomposes at 205—206°; the corresponding *picrate* crystallises from water and melts at 159—160°; the *platinichloride* crystallises in needles and melts at 206°. The above-described method gives an easy means of preparing 4-(or 5-)methylglyoxaline.

The production of methylglyoxaline from dextrose throws light on the origin of naturally occurring glyoxaline derivatives and on the transformation of dextrose into lactic acid. It is probable that the latter takes place through the primary formation of glyceric aldehyde and the subsequent transformation of this into methylglyoxal and lactic acid; that methylglyoxal is capable of being formed directly from dextrose is shown by the formation of methylglyoxaline, which probably occurs according to the equation $CH_3{\cdot}CO{\cdot}CHO + 2NH_3 + CH_2O \rightarrow \begin{matrix} CMe{\cdot}NH \\ \| \\ CH{-\!-}N \end{matrix}\!\!>\!CH$; the formaldehyde necessary may be either directly produced from the dextrose or by the decomposition of methylglyoxal, acetic acid being then also formed.

Among the other products of the action of ammoniacal zinc hydroxide on dextrose is the lactone saccharin, $C_6H_{10}O_5$. W. A. D.

Piperazine Glycerophosphates. A. Astruc (*Compt. rend.*, 1905, **140**, 727—730).—*Piperazine dihydrogen bisglycerophosphate*, $[PO(OH)_2{\cdot}O{\cdot}C_3H_5(OH)_2]_2,C_4H_{10}N_2,H_2O$, obtained as a transparent non-crystalline mass by evaporating an aqueous solution of glycerophosphoric acid (2 mols.) and piperazine (1 mol.), is neutral towards methyl-orange and acid towards phenolphthalein, and requires 3 mols. of an alkali to neutralise it in the presence of the latter indicator according to the equation $[PO(OH)_2O{\cdot}C_3H_5(OH)_2]_2,C_4H_{10}N_2 + 3MOH = PO(OM)_2{\cdot}O{\cdot}C_3H_5(OH)_2 + MO{\cdot}PO(OH{\cdot}C_4H_{10}N_2)O{\cdot}C_3H_5(OH)_2 + 3H_2O$.

Hydrogen piperazine glycerophosphate,

$$HO{\cdot}PO(OH{\cdot}C_4H_{10}N_2){\cdot}O{\cdot}C_3H_5(OH)_2,$$

obtained by mixing equivalent quantities of piperazine and glycerophosphoric acid in aqueous or alcoholic solution, crystallises in brilliant plates, melting and decomposing at 155°, readily soluble in water, and insoluble in absolute alcohol. It is alkaline towards methyl-orange and acid towards phenolphthalein, requiring 1 mol. of acid to render it neutral towards the former or 1 mol. of alkali to render it neutral towards the latter indicator. M. A. W.

Derivatives of 2:4-Diketotetrahydroquinazoline. Franz Kunckell (*Ber.*, 1905, **38**, 1212—1215).—2:4-*Diketo-3-bromophenyltetrahydroquinazoline* crystallises in colourless plates melting between 295° and 298°. 2:4-*Diketo-3-o-tolyltetrahydroquinazoline*,

$$C_6H_4\!<\!\begin{matrix} CO-N{\cdot}C_7H_7 \\ | \\ NH{\cdot}CO \end{matrix},$$

prepared by heating together anthranilic acid and *o*-tolylcarbamide at 165°, crystallises from alcohol in colourless, glistening plates melting at 243—244°; 2:4-*diketo-3-p-tolyltetrahydroquinazoline* forms colourless plates, which melt at 259—260°. By the interaction of anthranilic acid and guanidine carbonate, a colourless substance, $C_8H_7ON_3$, probably the 2-imino-4-ketotetrahydroquinazoline mentioned

by Griess (Abstr., 1880, 803), is obtained; this melts above 280° and can be sublimed. E. F. A.

Acetylation of Dihydrophenazine. MICHAEL M. TICHWINSKY and L. WOLOCHOWITSCH (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 8—11). —On acetylating dihydrophenazine, it yields *acetyldihydrophenazine*, $C_6H_5{<}{\genfrac{}{}{0pt}{}{NAc}{N\text{—}}}{>}C_6H_4$, which crystallises from alcohol or benzene in slender, colourless rhombohedra melting at 255° and difficultly soluble in all solvents. This same compound is obtained when phenazine is reduced in alcoholic ammonia solution and the product so obtained acetylated. Hence dihydrophenazine and, consequently, also phenazine must possess unsymmetrical formulæ. T. H. P.

m-**Tolylsemicarbazide.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 157572).—*m*-Tolylhydrazine hydrochloride reacts with potassium cyanate in cold aqueous solution to form *m*-tolylsemicarbazide: $C_6H_4Me{\cdot}NH{\cdot}NH_2,HCl + KCNO = C_6H_4Me{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2 + KCl$. m-*Tolylsemicarbazide* crystallises from hot water or dilute alcohol in white, glistening leaflets, melts at 183—184°, and dissolves sparingly in cold water or ether. Its solution reduces silver nitrate. Unlike the corresponding phenyl, *p*-tolyl and *o*-tolyl derivatives, it is tasteless and non-irritant.

In place of metallic cyanates, carbamide or ethyl carbamate may be employed in the preparation. C. H. D.

Condensation of ψ-Ammonium Bases with Hydroxylamine and *as*-Dimethyl-*p*-phenylenediamine. JOHANNES GADAMER (*Arch. Pharm.*, 1905, **243**, 43—49).—Experiments of a preliminary character have shown that the base of "crystal violet" does not condense with *p*-dimethylaminoaniline in ethereal solution, whereas those of quinoline methiodide and acridine methiodide appear to yield condensation products, and that of phenylacridine methiodide yields a product $C_{28}H_{27}N_3$ (probably $NMe_2{\cdot}C_6H_4{\cdot}N{:}CPh{\cdot}C_6H_4{\cdot}NMe{\cdot}C_6H_5$, derived from the ketonic form, $CPhO{\cdot}C_6H_4{\cdot}NMe{\cdot}C_6H_5$, of phenylmethylacridinium hydroxide, $C_6H_4{<}{\genfrac{}{}{0pt}{}{CPh\text{——}}{NMe(OH)}}{>}C_6H_4$), which melts at 188—189°. Phenylmethylacridinium hydroxide also forms with hydroxylamine in ethereal solution an *oxime* which has no sharp melting point; this is accompanied by a substance that is more soluble in ether, melts at 131°, and contains N 7·7 per cent. (possibly bisphenylmethylacridine hydroxylamine, derived from the tertiary carbinol form,

$$C_6H_4{<}{\genfrac{}{}{0pt}{}{CPh(OH)}{\text{—}NMe\text{—}}}{>}C_6H_4).$$

It would appear, therefore, that just those ψ-ammonium bases which, by the opening of a ring, can change into aldehydic or ketonic forms, do condense with *a* -dimethyl-*p*-phenylenediamine or hydroxylamine to form more or less stable products (compare this vol., i, 368).

C. F. B.

Desmotropic Compounds. OTTO DIMROTH (*Zeit. Elektrochem.*, 1905, **11**, 137—139).—The author fully admits the weight of Gold-

schmidt's criticisms (this vol., i, 249). He points out, however, the fact that the velocity of the change of the enolic form of methyl 5-hydroxy-1-phenyl-1 : 2 : 3-triazole-4-carboxylate into the ketoic form is greater in solvents with small dissociating power; for example, it is 10,000 times greater in chloroform solution than in aqueous solution. The change also occurs in the solid compound. It is therefore extremely probable that the change takes place within the undissociated molecule, and also that it has no connection with the formation of a hydrate. T. E.

Desmotropic Compounds. II. OTTO DIMROTH (*Annalen*, 1905, 338, 143—182. Compare Abstr., this vol., i, 98).—The investigation of the desmotropic change of methyl 5-hydroxy-1-phenyl-1 : 2 : 3-triazole-4-carboxylate into methyl 1-phenyl-5-triazolone-4-carboxylate (*loc. cit.*) has now been extended to the corresponding *p*-bromophenyl and *p*-tolyl derivatives, the ethyl esters being used instead of the methyl esters. The expressions $C_6H_4Br\cdot N<\begin{matrix}N=\!=\!=N\\ C(OH)\colon\dot{C}\cdot CO_2Et\end{matrix}$ and

$$C_6H_4Me\cdot N<\begin{matrix}N=\!=\!=N\\ C(OH)\colon\dot{C}\cdot CO_2Et\end{matrix}$$

represent respectively the enolic forms of these compounds. The enolic forms are colourless, of marked acid character, whilst the ketonic forms are yellow and neutral. The former change into the latter very slowly in the solid state, immediately on melting, and in solution with a velocity depending on the nature of the solvent. The ketonic esters are the stable form. The tolyl compound is a weaker, and the *p*-bromophenyl a stronger, acid than the phenyl derivative; the dissociation-constants are, respectively, tolyl, $100K = 1\cdot 0$; phenyl, $100K = 1\cdot 5$; and bromophenyl, $100K = 2\cdot 0$. The acids obtained from the esters are also desmotropic, the enolic acid being colourless and dibasic, and the ketonic yellow and monobasic. The enolic acid loses carbon dioxide, becoming converted into the triazole, but the ketonic acids yield respectively the *p*-bromoanilide and *p*-toluidide of glycollic acid.

The change of the enolic into the ketonic form is a unimolecular reaction. A table is given showing the relative values of the velocity constant k at 25° for the three hydroxytriazole derivatives.

The velocity of the change increases *pari passu* with the increase of strength of the acid; in all solvents, the phenyl derivative changes from 1·1 to 1·2 times more rapidly, and the bromophenyl from 4 to 5 times more rapidly than the tolyl compound. The velocity in all cases is smallest in water, and increases from methyl to ethyl alcohol and is greatest in acetone. Raising the temperature from 0° to 25° is accompanied by a great increase in the velocity in the ratio of 1 : 50 of the change in ethyl alcohol.

The proportion of enolic and ketonic forms present in equilibrium in methyl and ethyl alcohols has been estimated. In methyl alcohol, the proportion of enolic to ketonic form is, for the tolyl compound, 1/120, for the phenyl, 1/150, and for the bromophenyl, 1/555; in ethyl alcohol, the proportion is 1/230, 1/300 respectively for the two derivatives first mentioned. From these values, the velocity constant of

the change of the ketonic into the enolic form can be calculated. It is found that at 25° the velocity of this change is independent of the solvent and is the same for each of the three compounds, a fact which offers a remarkable contrast to the change of enol to ketone.

These results show that increase of the acidity of the enolic form is accompanied by an increase of the tendency to change into the ketonic form, a result in direct opposition to the behaviour of the di- and tri-ketones and to the desmotropy observed in the case of nitro-compounds.

[With H. STAHL.]—*Ethyl* 1-p-*tolyl*-5-*triazolone*-4-*carboxylate*,

$$C_6H_4Me\cdot N\begin{matrix}\diagup N{=}N \\ \diagdown CO\cdot \overset{|}{C}H\cdot CO_2Et\end{matrix},$$

is prepared by warming an alcoholic solution of *p*-tolyldiazoimide and ethyl sodiomalonate and decomposing the sodium salt of the enolic form, which separates with hydrochloric acid. On warming the enolic ester under water, it is converted into the ketonic form. The latter crystallises in yellow needles melting at 98—99°, and dissolves only gradually in alkali hydroxides, becoming thereby converted into the enolic form, from which it is distinguished by giving no coloration with ferric chloride and not setting free iodine from a solution of potassium iodate and iodide. The corresponding enolic *ethyl* 5-*hydroxy*-1-p-*tolyl*-1 : 2 : 3-*triazole*-4-*carboxylate* is obtained in the form of the sodium salt by treatment of a suspension of the ketone in alcohol with sodium ethoxide; the *salt* forms a white, crystalline powder soluble in water with a neutral reaction. When agitated with aqueous hydrochloric acid at 0°, the free enolic ester is formed as a white, crystalline powder, which, when kept in a desiccator in the dark, changes into the ketone very slowly, about 1·5 per cent. in the course of a week. If heated slowly, the colour changes to yellow and the melting point becomes that of the ketone, 98—99°. If heated suddenly to 90°, it melts, but not if heated to 88°. After melting at 90°, it immediately solidifies again, being converted into the ketonic ester. It can readily be titrated by potassium hydroxide in the presence of phenolphthalein or by estimating the iodine set free from a mixture of potassium iodate and iodide. The *ammonium* salt is a soluble, and the *silver* salt an insoluble, white powder. The *aniline* salt, $C_{18}H_{20}O_3N_4$, prepared by mixing cold alcoholic solutions of the base and the enol, crystallises in plates melting at 102°; the *phenylhydrazine* salt is a crystalline powder melting at 124·5°; the *benzidine* salt, $C_{36}H_{38}O_6N_8$, is a powder melting at 129°; the o-*tolidine* salt, $C_{38}H_{42}O_6N_8$, a crystalline powder melting at 119·5°, and the o-*anisidine* salt, $C_{38}H_{42}O_8N_8$, a grey powder melting at 112°. On melting, all these salts decompose into the free base and the ketonic form.

Ethyl 5-*methoxy*-1-p-*tolyl*-1 : 2 : 3-*triazole*-4-*carboxylate* is prepared from the silver salt of the enolic ester and methyl iodide in ethereal suspension, and forms cubical crystals melting at 68—69°. The *benzoxy*-compound is prepared from the silver salt and benzoyl chloride in absolute ether, and crystallises in needles and in compact crystals melting at 117—120°.

5-*Hydroxy*-1-p-*tolyl*-1 : 2 : 3-*triazole*-4-*carboxylic acid* is prepared by heating the ketonic ester with concentrated aqueous sodium hydroxide,

when the *di-sodium* salt, $C_{10}H_7O_3N_3Na_2$, of the enolic acid separates as a white, crystalline powder, easily soluble in water. The free *acid*, prepared by treatment of the sodium salt with hydrochloric acid at a low temperature, is a crystalline powder (with H_2O), melting and decomposing at 86—88°; it decomposes readily, losing carbon dioxide. The corresponding ketonic form, 1-p-*tolyl*-5-*triazolone*-4-*carboxylic acid*, $C_6H_4Me\cdot N<\begin{matrix}N=N\\ CO\cdot CH\cdot CO_2H\end{matrix}$, is obtained by keeping an ethereal solution of the enolic acid, and forms pale yellow, rhombic crystals sintering at 120° and melting at 175—180°; when heated, it gives a strong smell of carbylamine. 5-*Hydroxy*-1-p-*tolyl*-1 : 2 : 3-*triazole*,

$$C_6H_4Me\cdot N<\begin{matrix}N=\!=\!=N\\ C(OH):CH\end{matrix},$$

prepared by heating the enolic acid at 80° under water, crystallises in microscopic plates, melting and decomposing at 137°. When the ketonic acid is boiled with water, it quickly decomposes into glycollic-*p*-toluidide (m. p. 143°).

Ethyl 1-p-*bromophenyl*-5-*triazolone*-4-*carboxylate*,

$$C_6H_4Br\cdot N<\begin{matrix}N=N\\ CO\cdot C\cdot CO_2Et\end{matrix},$$

prepared from *p*-bromophenyldiazoimide and sodium ethoxide, crystallises in yellow needles melting at 138·5°. The *sodium* salt of the corresponding enol ester is prepared from the ketone by treatment with sodium ethoxide, and is converted by dilute hydrochloric acid at a low temperature into the free *enolic* ester, a white, crystalline powder, which changes so rapidly into the ketonic ester that the melting point cannot be determined. The *ammonium* salt is a white, crystalline powder, sintering at 180° and melting and decomposing at 182—183°; the *silver* salt is a white, insoluble powder. The *aniline* salt crystallises in white needles melting at 114—115°, the *phenylhydrazine* salt forms yellow crystals melting at 125°. The *benzidine* salt is a white, crystalline powder, the o-*tolidine* salt crystallises in needles melting at 110—118°, and the o-*anisidine* salt in small crystals melting at 88—89°.

Ethyl 5-*methoxy*-1-p-*bromophenyl*-1 : 2 : 3-*triazole*-4-*carboxylate*,

$$C_6H_4Br\cdot N<\begin{matrix}N=\!=\!=\!=N\\ C(OMe):C\cdot CO_2Et\end{matrix},$$

prepared from the silver salt, melts at 93°. The corresponding *benzoyloxy*-derivative crystallises in needles melting at 137°.

5-*Hydroxy*-1-p-*bromophenyl*-1 : 2 : 3-*triazole*-4-*carboxylic acid* is prepared by hydrolysing the ketonic ester with excess of sodium hydroxide, and then setting free the enolic acid from the di-sodium salt; it forms a white, crystalline powder with $2H_2O$, melting and decomposing at 96—100°. The *ketonic acid* is formed from the enol in ethereal solution, and crystallises in yellow needles melting and decomposing at 130°, the substance which is thus formed then melting at 207—208°. The enolic acid yields the corresponding 5-*hydroxy*-1-p-*bromophenyl*-1 : 2 : 3-*triazole*, which forms small crystals, melting and decomposing at 124°. The ketonic acid yields, on the other hand, *glycollic*-p-*bromoanilide*-

$C_6H_4Br{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}OH$, which crystallises in needles melting at 180°.

K. J. P. O.

Bistriazole Compounds. ERICH L. RINMAN (*Arkiv Kemi, Min., Geol.*, 1904, **1**, 221—263).—The author first gives an account of the bistriazole compounds already described and of the methods employed for preparing them.

The new bistriazole compounds described in the present paper have been obtained by means of cyanohydrazine (see Curtius, Abstr., 1895, i, 29), which has probably the constitution

$$NH_2{\cdot}N{:}C(NH_2){\cdot}C(NH_2){:}N{\cdot}NH_2.$$

When this compound is treated with an acid anhydride or chloride, it yields a condensation product of the formula $C_2(NH_2)_2({:}N{\cdot}NH{\cdot}CO{\cdot}R)_2$, and this, under the action of condensing agents, loses water and gives rise to a bistriazole compound. Condensation products containing different alkyl groups undergo conversion into bistriazole derivatives with varying degrees of ease and require, in some cases, acid condensing agents, and in others alkaline ones. The bistriazoles obtained form salts with both acids and bases, and all except phenylbistriazole yield well-defined crystalline platinichlorides of the type

$$(R{\cdot}C_2HN_3)_2,H_2PtCl_6,2H_2O.$$

Cyanohydrazine acts on ethyl chlorocarbonate, giving the compound $C_2(NH_2)_2({:}N{\cdot}NH{\cdot}CO_2Et)_2$, which, when treated with dilute potassium hydroxide solution, loses alcohol and condenses to bishydroxytriazole.

The oxidation of bismethyl- or bisethyl-triazole in alkaline solution yields potassium bistriazolecarboxylate,

$$CO_2K{\cdot}C\begin{matrix}\nearrow NH{\cdot}\overset{}{N}\quad \overset{}{N}{\cdot}NH\searrow \\ \qquad\ \ \Vert\quad \Vert \\ \searrow N - C{\cdot}C - N \nearrow\end{matrix}C{\cdot}CO_2K,$$

which yields an acetyl derivative of the constitution

$$OAc{\cdot}CO{\cdot}C\begin{matrix}\nearrow NAc{\cdot}N\quad N{\cdot}NAc\searrow \\ \qquad\ \ \Vert\quad \Vert \\ \searrow N - C{\cdot}C - N \nearrow\end{matrix}C{\cdot}CO{\cdot}OAc.$$

The author has synthesised cyanohydrazine by the action of hydrazine hydrate on dithio-oxamide, hydrogen sulphide being evolved and a practically quantitative yield of the cyanohydrazine being obtained.

On passing cyanogen into an aqueous solution of acetylhydrazide (Curtius, Abstr., 1895, i, 32), dicyanoacetylhydrazide is obtained. This compound can be converted into bismethyltriazole by two methods: (1) on heating its alcoholic solution in a sealed tube with acetylhydrazide, it yields a compound which is identical with that obtained by the interaction of acetic anhydride and cyanohydrazine and which, when boiled with acetic anhydride, gives bismethyltriazole. (2) It may be first converted into a monotriazole derivative and then into a bistriazole compound.

Bis-1-phenyl-3-triazole, $C_2N_3HPh{\cdot}C_2N_3HPh$, prepared by treating with water the product of the interaction of cyanophenylhydrazine and formic acid, separates from acetic acid in crystals melting at 277—278° and dissolving slightly in alcohol.

1-*Phenyl*-5-*methyl*-3-*triazenylamidrazone*,

$$NHPh{\cdot}N{:}C(NH_2){\cdot}C_2N_3PhMe,$$

obtained by acting with water on the product of the interaction of phenylmethyltriazenylamidoxime and an alcoholic solution of phenylhydrazine in a sealed tube, crystallises from alcohol in pale yellowish-brown prisms, which melt and decompose at 195°.

Bis-1-phenyl-5-methyl-3-triazole, $C_2N_3PhMe{\cdot}C_2N_3PhMe$, prepared by treating the preceding compound with acetic anhydride and acting on the product with dilute potassium hydroxide solution, separates in crystals which melt at 213—214°, but on subsequent heating, at 221—222° (compare Bladin, Abstr., 1889, 138).

Bis-3-triazole, $C_4H_4N_6$, prepared by the action of water on the condensation product of cyanohydrazine and formic acid, sublimes without melting at temperatures above 325° and dissolves in both acids and alkalis and to some extent in water. The *potassium*, *sodium*, *ammonium*, *copper*, and *silver* salts were prepared and the *hydrochloride*, which crystallises in shining, white leaves and readily loses its hydrogen chloride in the air; the *platinichloride*,

$$C_4H_4N_6,H_2PtCl_6,2H_2O,$$

separates in yellowish-red needles.

Bis-1-acetyl-3-triazole, $C_4H_2N_6Ac_2$, crystallises from a mixture of acetic acid and anhydride in spherical aggregates of white needles turning brown at about 225°.

Bis-5-methyl-3-triazole, $C_4H_2N_6Me_2$, separates from acetic acid in aggregates of small, white crystals, sublimes at above 325°, and dissolves readily in dilute mineral acids and to a slight extent in alcohol, water, or dilute acetic acid. The *potassium*, *sodium*, *ammonium* ($C_6H_{14}N_8$), and *silver* salts were prepared; the *hydrochloride*, $C_6H_8N_6,2HCl$, crystallises in small, colourless prisms and the *platinichloride* ($+ 2H_2O$) in large, yellowish-red prisms.

Bis-1-acetyl-5-methyl-3-triazole, $C_4N_6Me_2Ac_2$, crystallises from alcohol in slender, white needles melting and decomposing at about 230°.

Bis-5-ethyl-3-triazole, $C_4H_2N_6Et_2$, prepared from cyanohydrazine and propionic anhydride, separates from acetic acid in nodular crystals, sublimes at above 325°, and dissolves readily in dilute mineral acids and to a slight degree in water or alcohol. The *potassium*, *sodium*, and *ammonium* salts were prepared; the *hydrochloride* forms stable, thick, semi-translucent needles and the *platinichloride* ($+ 2H_2O$) separates in large, reddish-yellow crystals readily soluble in concentrated or dilute hydrochloric acids.

Bis-1-acetyl-5-ethyl-3-triazole, $C_4N_6Et_2Ac_2$, crystallises from alcohol in shining, white needles, melts at 185—186° and is decomposed by boiling water.

*Bis-5-*iso*propyl-3-triazole*, $C_4H_2N_6Pr^{\beta}_2$, prepared by heating the condensation product of di*iso*propylcyanohydrazine with sodium ethoxide in alcoholic solution, separates from alcohol in aggregates of small, colourless crystals, sublimes at above 325°, and dissolves readily in dilute mineral acids. The *potassium*, *sodium*, and *ammonium* salts were prepared; the *hydrochloride* forms aggregates of colourless crystals and the *platinichloride* separates from concentrated hydrochloric acid in large, reddish-yellow, anhydrous plates.

*Bis-1-acetyl-5-*iso*propyl-3-triazole*, $C_4N_6Pr^{\beta}_2Ac_2$, separates from alcohol in slender, white needles and melts at 200—202°.

Bis-5-phenyl-3-triazole, $C_4H_2N_6Ph_2$, crystallises from a mixture of acetic and concentrated hydrochloric acids in shining, microscopic needles, sublimes at above 325°, and dissolves slightly in acetic acid. The *potassium*, *sodium*, and *ammonium* salts were prepared; the *hydrochloride* ($+4H_2O$) forms microscopic needles decomposed by water.

Bis-1-acetyl-5-phenyl-3-triazole, $C_4N_6Ph_2Ac_2$, forms microscopic crystals with two rhombic surfaces and melting at 204—205°.

The condensation *product* of ethyl chlorocarbonate and cyanohydrazine (*vide supra*) crystallises from alcohol in microscopic, pointed needles which remain unchanged at 300°.

Bis-5-hydroxy-3-triazole, $C_4H_2N_6(OH)_2$, is obtained as a yellowish-white powder which is not changed at 325°.

Potassium bis-3-triazole-5-carboxylate, $C_4H_2N_6(CO_2K)_2,H_2O$, separates from water in shining, white needles.

Bis-3-triazole-5-carboxylic acid, $C_4H_2N_6(CO_2H)_2$, separates from acetic acid in microscopic crystals which remain unchanged at 325°. The *hydrochloride*, $C_4H_2N_6(CO_2H)_2,2HCl$, crystallises from a mixture of acetic and dilute hydrochloric acids in almost colourless leaflets. The *acetyl* derivative was prepared and the *benzoyl* derivative, which crystallises from water in pale greyish-yellow, three-sided prisms melting at 208—210°.

Dicyanoacetylhydrazide, $NHAc\cdot N{:}C(CN)\cdot NH_2$, crystallises from alcohol in yellowish-brown leaves melting and decomposing at 204—205°.

Diacetylcyanohydrazine, $NHAc\cdot N{:}C(NH_2)\cdot C(NH_2)\cdot N{:}NHAc$, crystallises from water in faintly translucent needles.

Dicyanoacetylhydrazideamidoxime, $NHAc\cdot N{:}C(NH_2)\cdot C(NH_2){:}NOH$, crystallises from water with H_2O in thin rods resembling mica which melt and decompose at 202°.

Methyltriazoleamidoxime, $C_2HN_3Me\cdot C(NH_2){:}N\cdot OH$, prepared by heating the preceding compound in a sealed tube with an alcoholic solution of sodium ethoxide, crystallises from water in colourless needles melting and decomposing at 212°.

Dicyanopropionylhydrazide, $COEt\cdot NH\cdot N{:}C(CN)\cdot NH_2$, separates from alcohol in a nodular, crystalline mass.

Dicyanobenzoylhydrazide, $NHBz\cdot N{:}C(CN)\cdot NH_2$, prepared by passing cyanogen into an aqueous solution of benzoylhydrazide, crystallises from alcohol in spherical aggregates of slender, yellowish-white needles melting and decomposing at 194—195°. T. H. P.

Hydroxyazo-compounds. HEINRICH GOLDSCHMIDT and OSCAR LÖW-BEER (*Ber.*, 1905, **38**, 1098—1113. Compare Abstr., 1890, 614; 1891, 1209; 1892, 974; McPherson, Abstr., 1896, i, 27; 1900, i, 123; Jacobson and Hönigsberger, Abstr., 1904, i, 205; Borsche, Abstr., 1904, i, 1056).—Phenylcarbimide reacts with *o*- and *p*-hydroxyazo-compounds to form carbamates which are insoluble in dilute alkali hydroxides. The carbamates derived from the *o*-hydroxyazo-compounds are reduced to hydrazo-compounds, which undergo the benzidine change, yielding diacid bases which are insoluble in dilute alkali hydroxides. These facts militate against the quinonehydrazone constitution for the hydroxyazo-compounds.

Carbanilido-*p*-hydroxyazobenzene is formed by the action of

phenylcarbimide on *p*-hydroxyazobenzene at the ordinary temperature; it crystallises in yellow needles and is now found to melt at 157°.

Carbo-p-toluidido-p-hydroxyazobenzene, $C_7H_7{\cdot}NH{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}N_2Ph$, formed from *p*-tolylcarbimide and *p*-hydroxyazobenzene, crystallises in yellow leaflets, melts at 170·5°, and is reduced by zinc dust and acetic acid in alcoholic solution to *carbo-p-toluidido-p-hydroxyhydrazobenzene*, $C_7H_7{\cdot}NH{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}NH{\cdot}NHPh$, which crystallises in small, colourless prisms, melts at 171°, and is insoluble in dilute alkali hydroxides. *Carbo-o-toluidido-p-hydroxyazobenzene* crystallises in slender, yellow needles, melts at 152°, and is reduced to *carbo-o-toluidido-p-hydroxyhydrazobenzene*, which crystallises in colourless needles and melts at 150°.

Benzeneazo-*p*-cresol reacts slowly with phenylcarbimide at the ordinary temperature to form *carbanilidobenzeneazo-p-cresol*,

$$NHPh{\cdot}CO{\cdot}O{\cdot}C_7H_6{\cdot}N_2Ph,$$

which decomposes into its generators when recrystallised from hot benzene; it is obtained by oxidation of the hydrazo-compound with mercuric oxide in ethereal solution in orange-red needles melting at 139°. *Carbanilidobenzenehydrazo-p-cresol* crystallises in nodular aggregates of colourless needles, melts at 157°, is insoluble in dilute alkali hydroxides, and when treated with concentrated hydrochloric acid in alcoholic solution yields *carbanilido-5-hydroxy-2-methylbenzidine*,

$$C_{20}H_{19}O_2N,$$

which crystallises from benzene, melts at 143—145°, and when boiled with aqueous sodium hydroxide is hydrolysed to aniline and a *substance* which is precipitated by carbon dioxide, but is soluble in mineral acids. The *hydrochloride*, $C_{20}H_{19}O_2N_3,2HCl$, crystallises in long, slender, colourless needles and melts at 291°.

Carbanilido-p-tolueneazo-p-cresol crystallises in orange-coloured needles, melts at 124°, and is reduced by zinc dust in alcoholic solution to *carbanilido-p-toluenehydrazo-p-cresol*, which crystallises in white needles and melts at 165°.

Carbanilido-m-chlorobenzeneazo-p-cresol crystallises in slender, orange-coloured needles, melts at 135—136°, and is soluble in the ordinary organic solvents. *Carbanilido-m-chlorobenzenehydrazo-p-cresol* crystallises in white needles, melts at 140°, is insoluble in cold dilute alkali hydroxides, and when treated with hydrochloric acid in alcoholic solution undergoes the benzidine change. The *base*, $C_{20}H_{16}O_2N_3Cl$, contains water of crystallisation, commences to sinter at 70°, and melts and decomposes at 140°; when anhydrous, it crystallises in white needles, melts at 134°, and, when boiled with aqueous sodium hydroxide, yields aniline and a *product* which is soluble in dilute alkali hydroxides and in dilute acids.

When reduced with zinc dust and acetic acid in alcoholic solution, the benzoyl derivative, obtained by the action of benzoic chloride on β-naphthaquinonephenylhydrazone or by the action of α-benzoylphenylhydrazine on β-naphthaquinone, yields β-benzenehydrazo-α-benzoylnaphthol, which crystallises in slender, colourless needles, melts and becomes red at 170°, is insoluble in dilute alkali hydroxides, and when treated with sodium hydroxide in alcoholic solution yields β-naphthaquinonephenylhydrazone. G. Y.

Azo-derivatives of Ethyl Oxalocrotonate. BERNHARDT PRAGER (*Annalen*, 1905, **338**, 360—392).—In order to study the resemblances and differences between a series of alternately singly and doubly linked carbon atoms in an open chain and in a closed ring, the formation of azo-derivatives from a phenol has been compared with their formation from unsaturated hydroxy-compounds. Diethyl oxalocrotonate (Lapworth, Trans., 1901, **79**, 1276), $CO_2Et\cdot C(OH)\dot{:}CH\cdot CH\dot{:}CH\cdot CO_2Et$, has been chosen as offering a series of CH groups related to an OH group, as are the ortho- and para-positions in phenol. It has been found that this compound yields readily both an azobenzene derivative and a dis-azo-derivative, thus: $CO_2Et\cdot C(OH)\dot{:}C(N_2\cdot C_6H_4Br)\cdot CH\dot{:}CH\cdot CO_2Et$ and $CO_2Et\cdot C(OH)\dot{:}C(N_2\cdot C_6H_4Br)\cdot CH\dot{:}C(N_2\cdot C_6H_4Br)\cdot CO_2Et$; it is seen that the monoazobenzene derivative is analogous to the *o*-phenolazobenzene, and not to the *para*-derivative, which is mainly formed in the case of phenol. Since diazobenzenes will not couple with ethyl crotonate or ethyl sorbate, the power to combine with diazobenzene is not due to the double bindings but to the hydroxyl group.

*Diethyl bis-*p*-bromobenzeneazo oxalocrotonate* is obtained by adding a solution of *p*-bromobenzenediazonium chloride to a solution of ethyl oxalocrotonate in a dilute solution of sodium carbonate, as an orange-red solid, which is purified by repeated extraction with small quantities of methyl alcohol and subsequent recrystallisation from alcohol; it forms crystals melting at 160°. The yellow alkaline mother liquor, from which the substance last mentioned separates, yields on acidification the *monoethyl ester* of *p*-bromobenzeneazo-oxalocrotonic acid,

$$CO_2Et\cdot CH\dot{:}CH\cdot C(N_2\cdot C_6H_4Br)\dot{:}C(OH)\cdot CO_2H,H_2O,$$

which crystallises in yellow needles, melting and decomposing at 122—123°. When 2 mols. of the *p*-bromodiazobenzene are used instead of one for each mol. of oxalocrotonate, no acid is formed and a somewhat better yield of the bis-azo-compound is obtained.

When the diazo-solution is added to an ammoniacal solution of the oxalocrotonate, a red precipitate separates, leaving a colourless mother liquor; this solid is *ethyl* 4 : 4′-*dibromoformazylacrylate*,

$$C_6H_4Br\cdot NH\cdot N\dot{:}C(N_2\cdot C_6H_4Br)\cdot CH\dot{:}CH\cdot CO_2Et,$$

which crystallises in needles melting at 150—151°. If a solution of benzenediazonium instead of *p*-bromobenzenediazonium chloride is used, the corresponding *ethyl formazylacrylate*, $C_{18}H_{18}O_2N_4$, is obtained as red needles melting at 128°. In both cases, alteration of the relative proportions of diazonium salt and oxalocrotonate does not affect the formation of the formazyl.

Diethyl p-*bromobenzeneazo-oxalocrotonate* is obtained when an acid solution of *p*-bromobenzenediazonium chloride in alcohol is added to an alcoholic solution of the oxalocrotonate; it crystallises in pale yellow prisms or needles melting at 125—126°, and dissolves very slowly in alkaline solutions. By use of excess of the diazonium salt, no dibenzeneazo-derivative was formed, but it is obtained if the monobenzeneazo-derivative is treated with *p*-bromodiazobenzene in acetic acid solution.

Since both the monoethyl *p*-bromobenzeneazo-oxalocrotonate and the diethyl ester, when treated with *p*-bromodiazobenzene in ammoniacal solution, yield the same ethyl dibromoformazylacrylate, it follows that

the benzeneazo-group is attached to the same carbon atom in the two compounds.

Diethyl p-*ethoxybenzeneazo-oxalocrotonate*,

$$CO_2Et\cdot C(OH):C(N_2\cdot C_6H_4\cdot OEt)\cdot CH:CH\cdot CO_2Et,H_2O,$$

is prepared from *p*-ethoxydiazobenzene and the oxalocrotonate in alcoholic solution, and crystallises in orange-yellow prisms melting at 85—86°. When treated with *p*-bromodiazobenzene in acetic acid solution, it is converted into *ethyl* p-*ethoxybenzeneazo*-p-*bromobenzeneazo-oxalocrotonate*,

$$CO_2Et\cdot C(OH):C(N_2\cdot C_6H_4\cdot OEt)\cdot CH:C(N_2\cdot C_6H_4Br)\cdot CO_2Et,$$

which crystallises in orange prisms melting at 160—161°; the isomeride, *ethyl* p-*bromobenzeneazo*-p-*ethoxybenzeneazo-oxalocrotonate*,

$$CO_2Et\cdot C(OH):C(N_2\cdot C_6H_4Br)\cdot CH:C(N_2\cdot C_6H_4\cdot OEt)\cdot CO_2Et,$$

is prepared from *p*-ethoxydiazobenzene and ethyl *p*-bromobenzeneazo-oxalocrotonate, and forms orange crystals melting at 169—170°, and is somewhat less soluble in all solvents than the isomeride.

Ethyl p-*bromobenzeneazo-oxaloacetate*,

$$CO_2Et\cdot CO\cdot CH(N_2\cdot C_6H_4Br)\cdot CO_2Et,$$

prepared from ethyl oxaloacetate and *p*-bromodiazobenzene in acetic acid solution, crystallises in yellow prisms melting at 93—94°, and is soluble in alkalis on warming. The corresponding formazyl, *ethyl* 4 : 4′-*dibromoformazylformate*, $C_6H_4Br\cdot NH\cdot N:C(N_2\cdot C_6H_4Br)\cdot CO_2Et$, is obtained by carrying out the coupling in the presence of ammonia, and crystallises in red needles melting at 158—160°; it is also formed from the ethyl *p*-bromobenzeneazo-oxaloacetate and *p*-bromodiazobenzene in acetic acid solution. K. J. P. O.

Azo-compounds of Phenylpyrazoles and their Halogen and Thio-derivatives. AUGUST MICHAELIS (*Annalen*, 1905, **338**, 183—235. Compare Abstr., 1904, i, 124).—A number of azopyrazoles are described which have been prepared from the corresponding benzeneazopyrazolones.

[With RICHARD LEONHARDT and KARL WAHLE.]—5-*Chloro*-1-*phenyl*-3-*methylpyrazole*-4-*azobenzene*, $N_2Ph\cdot C\Big<\begin{matrix}CCl-NPh\\CMe:\overset{|}{N}\end{matrix}$, is prepared from Knorr's phenylmethylpyrazoloneazobenzene by treatment with phosphorus oxychloride under pressure at 100°, and crystallises in slender, yellow needles melting at 109°; it is reconverted into the original substance by alcoholic potassium hydroxide, and with acid reducing agents yields 5-*chloro*-4-*amino*-1-*phenyl*-3-*methylpyrazole*,

$$NH_2\cdot C\Big<\begin{matrix}CCl-NPh\\CMe:\overset{|}{N}\end{matrix}.$$

The azo-compound gives with alcoholic silver nitrate an *additive compound*, $(C_{16}H_{13}N_4Cl)_2,AgNO_3$, which crystallises in yellow needles, melting at 132°, and is decomposed by hydrochloric acid. 5-*Iodo*-1-*phenyl*-3-*methylpyrazole*-4-*azobenzene* is obtained by the action of alcoholic potassium iodide on the chlorine compound and crystallises in reddish-yellow needles melting at 129°.

1-*Phenyl*-3-*methylpyrazole*-4-*azobenzene*, $N_2Ph\cdot C\Big<\begin{matrix}CH-NPh\\CMe:\overset{|}{N}\end{matrix}$, is pre-

pared by reducing the azochloro- or azoiodo-pyrazole with zinc dust and sodium hydroxide in alcoholic solution, and crystallises in reddish-yellow leaflets melting at 126°; it yields an unstable *hydrochloride* crystallising in red needles melting and decomposing at 114°.

1-*Phenyl*-3-*methyl*-5-*thiopyrazolone*-4-*azobenzene*,

$$N_2Ph\cdot CH{<}\begin{matrix}CS-NPh\\ CMe:N\end{matrix},$$

is prepared by heating the chloroazopyrazole with sulphide of potassium or sodium in alcoholic solution, a salt of the thio-compound being first obtained; the substance crystallises in dark red needles melting at 97°, behaves as a weak base, and is soluble in alkali hydroxides, but not in carbonates; it is reduced to a colourless substance by acid reducing agents. The *mercury mercaptide* is obtained by adding mercuric oxide to a boiling solution of the azothiopyrazolone in toluene, and crystallises in brick-red needles melting at 228°. The *mercurichloride*, $N_2Ph\cdot C{<}\begin{matrix}C(S\cdot HgCl)\cdot NPh\\ CMe{=}{=}{=}{=}N\end{matrix}$, prepared by mixing a hot alcoholic solution of mercuric chloride and the azothiopyrazolone, crystallises in yellow needles melting at 217°.

5-*Thiomethyl*-1-*phenyl*-3-*methylpyrazole*-4-*azobenzene*, prepared by treating the azothiopyrazolone with methyl iodide in the presence of alcoholic potassium hydroxide, crystallises in reddish-yellow needles melting at 63° and is readily oxidised by permanganate to the corresponding *sulphone*, $N_2Ph\cdot C{<}\begin{matrix}C(SO_2Me)\cdot NPh\\ CMe{=}{=}{=}{=}N\end{matrix}$, which crystallises in reddish-yellow needles melting at 156°. The 5-*thioethyl-pyrazole*, prepared in like manner to the methyl derivative, crystallises in reddish-yellow needles melting at 71°; it can also be obtained from 5-chloro-1-phenyl-3-methyl-4-azobenzene and sodium mercaptide. The 5-*thiophenyl-pyrazole* is obtained from the chloroazopyrazole and thiophenol in the presence of sodium ethoxide, and crystallises in yellowish-red plates or prisms melting at 115°; the *sulphone*, obtained from it by oxidation with permanganate in acetic acid solution, forms scarlet crystals melting at 145°. When the sodium salt of the azothiopyrazolone is shaken with benzoyl chloride, the *thiobenzoate* is formed as red needles melting at 127°. Monochloroacetic acid reacts with an alkaline solution of the azothiopyrazolone giving a 4-*benzeneazo*-1-*phenyl*-3-*methylpyrazole*-5-*thioglycollic acid*, $N_2Ph\cdot C{<}\begin{matrix}C(S\cdot CH_2\cdot CO_2H)\cdot NPh\\ CMe{=}{=}{=}{=}{=}{=}N\end{matrix}$, crystallising in pale yellow needles melting at 166°; its *silver* salt crystallises in red needles melting and decomposing at 193°.

1-*Phenyl*-3-*methylpyrazole*-4-*azobenzene*-5-*sulphide*,

$$\left(\begin{matrix}CMe\cdot C(N_2\cdot Ph)\\ N{-}{-}{-}{-}{-}NPh\end{matrix}{>}C\cdot\right)_2S,$$

is prepared by heating together molecular proportions of 5-chloroazopyrazole and 4-azothiopyrazolone at 100°, and crystallises in pale reddish-yellow needles melting at 86°; the corresponding *disulphide* is obtained by the action of iodine on a solution of the mercury salt of azothiopyrazolone in toluene, and crystallises in dark yellow, rhombic prisms melting at 115°.

5-*Chloro*-1-*phenyl*-3-*methylpyrazole*-4-o-*azotoluene*,

$$C_6H_4Me\cdot N_2\cdot C{<}\begin{matrix}CCl-NPh\\ CMe:N\end{matrix},$$

prepared by the action of phosphorus oxychloride on the corresponding pyrazolone, crystallises in yellow needles melting at 94°. 1-*Phenyl*-3-*methyl*-5-*pyrazolone*-o-*azotoluene* is prepared by adding a solution of *o*-toluenediazonium chloride in hydrochloric acid to a solution of phenylmethylpyrazolone in acetic acid; it crystallises in red needles melting at 185°. The chloro-compound is reduced by zinc dust and sodium hydroxide to the corresponding *pyrazole*-o-*azotoluene*,

$$C_6H_4Me\cdot N_2\cdot C{<}\begin{matrix}CH-NPh\\ CMe:N\end{matrix},$$

which forms golden-yellow leaflets melting at 91°; the *hydrochloride* crystallises in red needles. 5-*Thiol*-1-*phenyl*-3-*methylpyrazolone*-4-o-*toluene* crystallises in dark red needles melting at 136°.

1-*Phenyl*-3-*methylpyrazolone*-p-*azotoluene*,

$$C_6H_4Me\cdot N_2\cdot CH{<}\begin{matrix}CO-NPh\\ CMe:N\end{matrix},$$

is prepared in similar manner to the corresponding *ortho*-compound crystallises in red needles melting at 141°, and yields with phosphorus oxychloride the 5-*chloro*-compound, which forms yellow needles melting at 118°. On reduction, it gives the corresponding *pyrazole*, which crystallises in yellow leaflets melting at 84°. The *thiopyrazolone* crystallises in dark red needles melting at 123°.

5-*Chloro*-1-p-*tolyl*-3-*methylpyrazole*-4-*azobenzene*,

$$N_2Ph\cdot C{<}\begin{matrix}CCl-N\cdot C_6H_4Me\\ CMe:N\end{matrix},$$

prepared by the action of phosphorus oxychloride on 1-*p*-tolyl-3-methyl-5-pyrazolone-4-azobenzene, crystallises in yellow needles melting at 107°. When oxidised by chromic acid in the presence of sulphuric acid, it is converted into 5-*chloro*-4-*benzeneazo*-3-*methylpyrazole*-1-p-*benzoic acid*, $N_2Ph\cdot C{<}\begin{matrix}CCl-N\cdot C_6H_4\cdot CO_2H\\ CMe:N\end{matrix}$, which is a brown, insoluble powder. The chloropyrazole yields an *additive* compound with silver nitrate, $(C_{17}H_{15}N_4Cl)_2,AgNO_3$, which crystallises in yellow needles melting at 193—194°. 1-p-*Tolyl*-3-*methylpyrazole*-4-*azobenzene*, prepared by reducing the chloro-compound with zinc dust and sodium hydroxide, crystallises in pale yellow needles melting at 83°; its *hydrochloride* is colourless and unstable.

5-*Thio*-1-p-*tolyl*-3-*methylpyrazolone*-4-*azobenzene*,

$$N_2Ph\cdot CH{<}\begin{matrix}CS-N\cdot C_6H_4Me\\ CMe:N\end{matrix},$$

prepared from the chloropyrazole, crystallises in dark red needles melting at 116°, and when warmed with dilute nitric acid is converted into 5-*nitro*-1-p-*tolyl*-3-*pyrazole*-4-*azobenzene*, which crystallises in dark red needles melting at 132° and is insoluble in acids or alkali hydroxides. The *mercury mercaptide* crystallises in yellowish-red needles melting at 226°, and the *mercurichloride*, $N_2Ph\cdot C{<}\begin{matrix}C(S\cdot HgCl)\cdot N\cdot C_6H_4Me\\ CMe{=\!=}N\end{matrix}$, in

yellow needles melting at 236°. The *thiomethyl ether* forms dark yellow crystals melting at 82° and the *thioethyl ether* yellow crystals melting at 61° and the *thiophenyl ether* red prisms or plates melting at 108°, which, when oxidised, is converted into the *phenylsulphone* crystallising in reddish-yellow prisms melting at 146°. The *thiobenzoate*,

$$N_2Ph\cdot C\Big\langle{C(SBz)\cdot N\cdot C_6H_4Me \atop CMe \!=\! N},$$

obtained from an alkaline solution by use of benzoyl chloride, crystallises in orange-red needles melting at 121°, and the *thioglycollic acid*, $N_2Ph\cdot C\Big\langle{C(S\cdot CH_2\cdot CO_2H)\cdot N\cdot C_6H_4Me \atop CMe \!=\!=\!=\! N}$, yellowish-brown needles melting at 159°. Its *barium* salt forms pale yellow needles decomposing at 230°. 1-p-*Tolyl*-3-*methylpyrazole*-4-*azobenzene*-5-*sulphide*,

$$\left(\begin{matrix} CMe\cdot C(N_2Ph) \\ N\cdot N(C_6H_4Me) \end{matrix}\!\!>\!C\right)_2S,$$

prepared from the chloropyrazole, crystallises in yellow needles melting at 106°.

5-*Chloro*-1-p-*tolyl*-3-*methylpyrazole*-4-p-*azotoluene*,

$$C_6H_4Me\cdot N_2\cdot C\Big\langle{CCl-N\cdot C_6H_4Me \atop CMe{:}N},$$

prepared in the usual manner, crystallises in yellow needles or leaflets melting at 155—156°, and on reduction yields the corresponding *pyrazole*, which forms dark yellow leaflets melting at 121°; its *hydrochloride* crystallises in red, unstable needles. 5-*Thio*-1-p-*tolyl*-3-*methylpyrazolone*-4-p *azotoluene*, $C_6H_4Me\cdot N_2\cdot CH\Big\langle{CS-N\cdot C_6H_4Me \atop CMe{:}N}$, crystallises in lustrous, dark red leaflets melting at 174°.

[With Heinrich Simon.]—3 : 5-*Dichloro*-1-*phenylpyrazole*-4-*azobenzene*, $N_2Ph\cdot C\Big\langle{CCl-NPh \atop CMe{:}N}$, prepared from 3-hydroxy-1-phenyl-5-pyrazolone-4-azobenzene and phosphorus oxychloride, crystallises in needles melting at 115°, and when treated with alcoholic potassium hydroxide is converted into 3-*chloro*-1-*phenyl*-5-*pyrazolone*-4-*azobenzene*,

$$N_2Ph\cdot CH\Big\langle{CO-NPh \atop CCl{:}N},$$

the chlorine in position 5 being in all reactions the more easily replaced; the pyrazolone crystallises in purplish-red needles melting at 164°, and can also be prepared from 3-chloro-1-phenyl-5-pyrazolone and benzenediazonium chloride. 3-*Chloro*-1-*phenylpyrazole*-4-*azobenzene* is obtained by reduction of the dichloro-compound, and crystallises in yellow needles melting at 140°. 3-*Chloro*-5-*thio*-1-*phenylpyrazolone*-4-*azobenzene*,

$$N_2Ph\cdot CH\Big\langle{CS-NPh \atop CCl{:}N},$$

is prepared from the dichloro-compound and sodium or ammonium sulphide, and crystallises in reddish-brown needles melting at 138°.

3 : 5-*Dichloro*-1-*phenylpyrazole*-4-p-*azotoluene*,

$$C_6H_4Me\cdot N_2\cdot C\Big\langle{CCl\cdot NPh \atop CCl{:}N},$$

prepared in a manner similar to that described above, crystallises in

needles melting at 112°. When warmed with potassium iodide solution on the water-bath, 3-*chloro*-5-*iodo*-1-*phenylpyrazole*-4-p-*azotoluene* is obtained as orange-yellow leaflets melting at 143°. On treatment with alcoholic potassium hydroxide, the dichloro-compound yields 3-*chloro*-1-*phenyl*-5-*pyrazolone*-4-p-*azotoluene*, crystallising in red needles which melt at 85°. The corresponding 3-*chloro*-1-*phenylpyrazole*-4-p-*azotoluene* crystallises in lemon-yellow needles melting at 106°. 3-*Chloro*-5-*thio*-1-*phenylpyrazolone*-4-p-*azotoluene* crystallises in needles melting at 146°. 3-*Bis*-5-*thio*-1-*phenylpyrazolone*-4-p-*azotoluene*, prepared from the compound last mentioned by prolonged heating with an alkali, forms dark red crystals melting at 232°. The *mercurichloride*, $C_6H_4Me\cdot N_2\cdot C\Big<\begin{matrix}C(S\cdot HgCl)\cdot NPh\\ CCl=\!=\!=N\end{matrix}$, obtained when the corresponding thiopyrazolone is treated with alcoholic mercuric chloride, crystallises in pale yellow needles melting at 232°. The *thiomethyl-pyrazole*,

$$C_6H_4Me\cdot N_2\cdot C\Big<\begin{matrix}C(SMe)\cdot NPh\\ CCl=\!=\!=N\end{matrix},$$

prepared from the chlorothiopyrazolone and methyl iodide in the presence of alcoholic potassium hydroxide, crystallises in golden-yellow leaflets melting at 109°, and is oxidised to the corresponding *sulphone* by permanganate in acetic acid solution; the latter crystallises in yellow needles melting at 152°. The *thioethyl-pyrazole* crystallises in golden-yellow needles melting at 112°. The *thiobenzoate*, $C_6H_4Me\cdot N_2\cdot C\Big<\begin{matrix}C(SBz)\cdot NPh\\ CCl=\!=\!=N\end{matrix}$, crystallises in yellowish-red needles melting at 125°. 1-*Phenyl*-3-*chloropyrazole*-4-p-*azotoluene*-5-*sulphide* is prepared by heating a mixture of 3 : 5-dichloro-1-phenyl-4-*p*-azotoluene and the chlorothiopyrazolone and crystallises in yellow needles melting at 180°.

[With Johann Behrens.]—The azo-compounds of 1-phenyl-5-methyl-3-pyrazolone are prepared in the usual manner; 1-*phenyl*-5-*methyl*-3-*pyrazolone*-4-*azobenzene*, $N_2Ph\cdot C\Big<\begin{matrix}CMe\cdot NPh\\ CO-NH\end{matrix}$, crystallises in dark yellow leaflets or needles melting at 99—100°; its *sodium* salt is a red, crystalline powder melting at 207°, and its *hydrochloride* forms red needles melting at 147—149°. The *benzenesulphonyl* derivative, $N_2Ph\cdot C\Big<\begin{matrix}CMe-\!\!-NPh\\ C(SO_3Ph):N\end{matrix}$, prepared by shaking an alkaline solution of the azopyrazolone with benzenesulphonic chloride, crystallises in yellow needles melting at 132°. With phosphorus oxychloride, the azopyrazolone yields 3-*chloro*-1-*phenyl*-5-*methylpyrazole*-4-*azobenzene*, $N_2Ph\cdot C\Big<\begin{matrix}CMe\cdot NPh\\ CCl=N\end{matrix}$, which crystallises in yellow needles melting at 90°.

1-p-*Tolyl*-5-*methyl*-3-*pyrazolone*-4-*azobenzene*,

$$N_2Ph\cdot C\Big<\begin{matrix}CMe\cdot N\cdot C_6H_4Me\\ CO-NH\end{matrix},$$

crystallises in brownish-yellow leaflets melting at 169°, and the corresponding *o*-tolyl derivative in yellowish-brown needles melting at

130°. The *sodium* salts of both compounds are red, crystalline powders. The *hydrochloride* of the *o*-tolyl compound is easily, but that of the *p*-tolyl compound sparingly, soluble; both form red needles. The *benzenesulphonyl* derivative of the *p*-tolyl compound crystallises in yellow needles melting at 112°, and that of the *o*-tolyl compound in yellow needles melting at 113°. 3-*Chloro*-1-p-*tolyl*-5-*methylpyrazole*-4-*azobenzene*, prepared by the action of phosphorus oxychloride on the 3-pyrazolone, forms pale red crystals melting at 103°. K. J. P. O.

Diazoamino-compounds derived from Diphenylamine and the Homologues of Aniline and the Naphthylamines. Léo Vignon and Adolphe Simonet (*Compt. rend.*, 1905, **140**, 788—790. Compare Abstr., 1904, i, 637, 1065).—The compound, $NPh:N\cdot NPh_2$, obtained by diazotising aniline in presence of diphenylamine has been already described. The three toluidines, three xylidines, and the two naphthylamines have now been treated in a similar manner. The substance obtained from *o*-toluidine, $C_6H_4Me\cdot N:N\cdot NPh_2$, is a fairly stable oil of a red colour, very soluble in alcohol and ether, insoluble in water.

The *m*-toluidine derivative is a reddish-brown powder which crystallises readily from alcohol and decomposes at 135—140°. From *p*-toluidine, an unstable, reddish-brown oil is obtained which gives off nitrogen at the ordinary temperature.

From 1 : 2 : 3-xylidine, an oil is obtained which solidifies after several days, then melts at 100—110°, and decomposes at 125°. No definite products were obtainable from 1 : 2 : 4- and 1 : 4 : 3-xylidines. When α-naphthylamine is diazotised in presence of diphenylamine, the latter takes no part in the reaction. If α-naphthalenediazonium chloride is first prepared and treated with diphenylamine in alcoholic solution, a dark-coloured oil is obtained which is probably diphenylaminodiazonaphthalene. It gives off nitrogen and decomposes according to the equation $C_{10}H_7N:N\cdot NPh_2 + H_2O = C_{10}H_7\cdot OH + NHPh_2 + N_2$. β-Naphthylamine behaves in a similar manner to the α-compound. The three monoaminophenols, *o*-aminobenzoic acid, and *o*-aminosalicylic acid do not yield diphenylaminodiazo-derivatives under the conditions described. H. M. D.

Action of Chloroform on Proteids. E. S. Edie (*Thompson, Yates, and Johnston Lab. Rep., Liverpool*, 1905, **6**, 195—200).—The proteids investigated were those of serum and hæmoglobin, in reference to the work of Moore and Roaf (see this vol., ii, 272). The compound of chloroform and hæmoglobin is less stable than carboxyhæmoglobin. When sufficient chloroform is added to produce precipitation, the amount of chloroform found in the precipitate is constant. In the case of the serum proteids also, the amount of chloroform is fairly constant. W. D. H.

A Globulin occurring in the Chestnut. William E. Barlow (*J. Amer. Chem. Soc.*, 1905, **27**, 274—276).—A globulin has been obtained from the edible Spanish chestnut (*Castanea vesca*) by extraction with 10 per cent. sodium chloride solution; this, when dry, forms a grey powder, and under certain conditions separates as minute plates, bounded by three curved edges. The proteid is insoluble

in water, but is readily soluble in 10 per cent. sodium chloride solution, and is reprecipitated by ammonium sulphate, dilute hydrochloric acid, or acetic acid.

When a saline solution of the globulin is heated, it becomes opalescent at 74—75°, and is only partially precipitated on boiling; on adding a trace of hydrochloric acid to the hot solution, however, complete precipitation of the proteid takes place. In most of its reactions, this proteid resembles corylin, the globulin of the filbert, but differs from it in its temperature of coagulation and its precipitation limits with ammonium sulphate. The substance is probably not identical with any of the vegetable proteids previously isolated and is provisionally termed *castanin*. E. G.

Hydrolysis of Proteids. II. Gelatin. ZDENKO H. SKRAUP (*Monatsh.*, 1905, **26**, 243—264. Compare Abstr., 1904, i, 538, 594; Siegfried, Abstr., 1903, i, 586).—Gelatin was hydrolysed by 12·5 per cent. hydrochloric acid at 39° for 12 days and the products isolated by addition of phosphotungstic acid, filtration of the amorphous precipitate, and evaporation of the filtrate.

On recrystallisation of the amorphous precipitate, a small amount of a crystalline phosphotungstate was obtained. The least soluble part of this yielded an *acid*, $C_{12}H_{25}O_{10}N_5$, which crystallises in long, thin, microscopic prisms, melts at 251—253°, and is easily soluble in hot water. The *ammonium* salt crystallises in microscopic plates; the *copper* salt, $C_{12}H_{19}O_{10}N_5Cu_3,5H_2O$, forms long, blue prisms and loses $3H_2O$ at 130°. The moderately soluble part of the phosphotungstate formed stellate aggregates of slender needles and is probably Siegfried's glutokyrine phosphotungstate. The most soluble fraction of the phosphotungstate yielded diaminoglutaric acid. The filtrate from the amorphous precipitate yields glycine, diaminoglutaric acid, and an acid, $C_4H_7O_4N$, which decomposes without melting at 220° and forms a bluish-green copper salt. Aminohydroxysuccinic, diaminodihydroxysuberic, and caseanic acids were not found amongst the hydrolysis products.

Glycine and diaminoglutaric acid, which are found in gelatin in much larger quantity than in casein, form a salt, $(C_2H_4O_2N)_2,C_5H_{10}O_4N_2$, which crystallises in microscopic prisms and melts and decomposes at 238—239°. G. Y.

Thymonucleic Acids. II. HERMANN STEUDEL (*Zeit. physiol. Chem.*, 1905, **43**, 402—405. Compare Abstr., 1904, i, 837).—The results obtained by the hydrolysis of copper thymonucleate with various reagents are tabulated as follows, when the total nitrogen = 100.

	Hydrolytic agent.		
Nitrogen in form of	Hydriodic acid.	Sulphuric acid.	Hydrochloric acid and stannous chloride.
Ammonia	7·00	5·20	16·08
Humin	11·54	6·58	—
Guanine	3·61	10·07	3·15
Adenine	13·45	16·39	4·76
Cytosine	11·45	11·47	10·15
Thymine	15·88	13·11	11·91

The results indicate that sulphuric acid is the best hydrolytic agent, as it produces less complex decomposition. J. J. S.

Spectroscopic Study of Oxyhæmoglobin. M. PIETTRE and A. VILA (*Compt. rend.*, 1905, **140**, 685—687).—It has been found that the absorption spectrum of aqueous solutions of crystallised oxyhæmoglobin is altered on the addition of certain substances to the solutions

The absorption band ($\lambda = 634$) is particularly sensitive, and the substances which displace or suppress this band are such as are usually regarded as having no action on the colouring matter of the blood. Sodium chloride in eight per cent. solution suppresses the band, and under certain conditions causes a thin band at $\lambda = 597$ to make its appearance. The alkali fluorides and hydrofluoric acid displace the band to the position $\lambda = 612$. The free acid produces this effect in very dilute solution, and is still more active at 38° than at 20°. Potassium chloride, bromide, and iodide have no action, and this is also the case for sodium bromide and iodide. The absorption band is suppressed by the alkalis and by sodium hydrogen carbonate, but not by dilute solutions of acids such as acetic and carbonic. It is intensified by alkali sulphates and magnesium sulphate.

H. M. D.

Modification of the Spectrum of Methæmoglobin under the Action of Sodium Fluoride. JULES VILLE and EUGÈNE DERRIEN (*Compt. rend.*, 1905, **140**, 743—744).—The addition of a freshly prepared solution of sodium fluoride to a solution of methæmoglobin or methæmoglobinised blood causes the band in the red having its centre at $\lambda = 633$, characteristic of methæmoglobin, to disappear, whilst a new band is formed, having its centre at $\lambda = 612$. The same results have been obtained with blood methæmoglobinised by means of potassium ferricyanide, sodium nitrite, or hydrogenised palladium, with solutions of oxyhæmoglobin partially methæmoglobinised by spontaneous change, or with solutions of crystallised methæmoglobin. The change in the spectrum of oxyhæmoglobin observed by Piettre and Vila (preceding abstract) was probably due to a partial methæmoglobinisation of the colouring matter of the blood. M. A. W.

Colouring Matter of Blood. IV. H. GOLDMANN and LEON MARCHLEWSKI (*Zeit. physiol. Chem.*, 1905, **43**, 415—416).—Hæmopyrrole readily couples with an aqueous solution of benzenediazonium chloride, yielding an *azo-dye* which crystallises in brown needles melting at 241·5°. It is sparingly soluble in ether, toluene, boiling dilute hydrochloric acid, or alkali hydroxides, but dissolves readily in alcohol, yielding cherry-red solutions, in chloroform, or in concentrated sulphuric acid to bluish-violet solutions. J. J. S.

Colouring Matter of Blood. III. JOZEF BURACZEWSKI and LEON MARCHLEWSKI (*Zeit. physiol. Chem.*, 1905, **43**, 410—414).—Attempts have been made to synthesise hæmopyrrole (Nencki and Zaleski, Abstr., 1901, i, 434; Küster, *ibid.*, 1902, i, 845; Küster and Hass, *ibid.*, 1904, i, 647) by distilling α-methyl-β-propylmaleinimide

(Abstr., 1904, i, 648) with zinc dust in an atmosphere of hydrogen. After exposure to the air, a reddish-brown dye was obtained, which was soluble in alcohol and closely resembled urobilin.

Synthetical methylmalic acid has been resolved into its optically active components by means of strychnine, the salt of which with the *d*-acid is sparingly soluble. The *d*-acid crystallises from ethyl acetate, melts at 108—109°, and has $[\alpha]_D + 22 \cdot 83°$ at 20° ($c = 1 \cdot 5$).

The hæmin crystals obtained by means of propionic acid (*Bull. Acad. Sci. Cracow*, 1904, 224) are crystallographically identical with those examined by Lagorio (Schalféeff, Abstr., 1885, 566). J. J. S.

Reduced Acid Hæmatin. S. A. Milroy (*Proc. Physiol. Soc.*, 1904—1905, xii—xiv; *J. Physiol.*, **32**).—Reduced acid hæmatin may be obtained by the use of feeble reducing agents in the cold. If a small amount of zinc dust is added to a solution of hæmatin in glacial acetic acid, the lower layer becomes bright red, but on shaking it with air it again becomes brown. But zinc dust thus used is too powerful, and some hæmatoporphyrin is formed. Better results are obtained by using a solution of hæmatin in alcohol containing 0·4 to 0·8 per cent. of oxalic acid; a trace of zinc dust is added, and reduction occurs slowly, air having first been displaced by a current of hydrogen. The red solution so formed shows a single absorption band between D and E. If a current of carbon monoxide is used instead of hydrogen, a compound is formed with two bands. A similar compound with nitric oxide was also obtained. W. D. H.

Catalases. Hans Euler (*Arkiv Kem. Min. Geol.*, 1904, **1**, 357—364).—By Senter's method (Abstr., 1903, ii, 661), pure catalase was prepared from blood, and its action is compared with that of fat catalases. Fat catalase is much less sensitive to the action of acids and bases; their influence is dependent on their concentrations. W. D. H.

Action of Sulphuryl Chloride on Mixed Organo-magnesium Compounds. Bernardo Oddo (*Atti R. Accad. Lincei*, 1905, [v], **14**, i, 169—174).—The action of sulphuryl chloride on magnesium phenyl bromide mainly proceeds in two stages, in the first of which the chloride of benzenesulphinic acid is formed: (1) $SO_2Cl_2 + MgBrPh = MgBrCl + SO_2PhCl$; (2) $SO_2PhCl + MgBrPh = PhCl + O{:}SPh{\cdot}OMgBr$. The last compound, when treated with water, yields benzenesulphinic acid.

There are also formed small amounts of chlorobenzene and diphenyl, the latter resulting from a secondary reaction: $MgBrPh + C_6H_5Br = C_6H_5{\cdot}C_6H_5 + MgBr_2$. This secondary reaction increases in amount as the complexity of the alkyl group in the organo-magnesium compound increases. T. H. P.

Organic Chemistry.

General Methods of Hydrogenation and Decomposition based on the Use of Finely-divided Metals. Part II. Molecular Decompositions and Condensations. Paul Sabatier and Jean B. Senderens (*Ann. Chim. Phys.*, 1905, [viii], 4, 433—488).—This is a general discussion of the mechanism of the action of metals in a finely-divided condition on various classes of organic compounds, in which the results recorded in the following abstracts are used as illustrations: Abstr., 1897, i, 305, 545; 1899, i, 555; 1900, i, 197, 421, 470, 471, 534; 1901, i, 195, 263, 459, 638; 1902, i, 525, 581, 701; 1903, i, 393, 453, 454, 686, 733; 1904, i, 156, 277, 303, 305, 660, and this vol., i, 254, 267. It is shown that the reactions, other than direct hydrogenation, which go on in these cases are due either to the initial formation of unstable metallic hydrides or to the combination of the metals with the organic substances employed or their decomposition products.

It is pointed out that the action of gaseous hydrogen in presence of finely-divided nickel, maintained at 250°, is capable of general application for the reduction of volatile substances, and that the passage of the vapours of primary and secondary alcohols over heated finely-divided copper is a convenient method of preparing the corresponding aldehydes and ketones. T. A. H.

Employment of Metalammonium Compounds in Organic Chemistry; Preparation of Fatty Hydrocarbons. Paul Lebeau (*Compt. rend.*, 1905, **140**, 1042—1044).—When the halogen substitution products of the fatty hydrocarbons are brought into contact with the blue solution of sodammonium obtained by passing perfectly dry ammonia into a tube containing sodium cooled by means of solid carbon dioxide and acetone, the corresponding hydrocarbons are obtained. When a current of methyl chloride vapour is passed into the solution, the blue colour gradually disappears and methane is evolved. Ethyl iodide and propyl iodide, when allowed to drop slowly into the solution, give rise to ethane and propane respectively. Calcium ammonium reacts in the same manner as sodammonium. If the substances employed are not perfectly dry, hydrogen is evolved. The change cannot be attributed to the action of the alkali (or alkaline earth) metal, for the products are quite different from those obtained by the reactions of Wurtz or Frankland. Polysubstituted halogen derivatives of both fatty and aromatic hydrocarbons are found to react similarly. H. M. D.

Liquefaction of Allene and Allylene. Robert Lespieau and G. Chavanne (*Compt. rend.*, 1905, **140**, 1035—1036).—Allene, $CH_2\colon C\colon CH_2$, prepared by the action of powdered zinc on α-epidibromohydrin in presence of alcohol and purified by repeated washing with

water and drying over calcium chloride and fused potassium hydroxide, was solidified and distilled in a vacuum. The first portion of the distillate thus obtained was used for the investigation. It melts at $-146°$, and its vapour pressure at this temperature is 10 mm. It boils at $-32°$ under 760 mm. pressure; its critical temperature is 120·75°.

Allylene, $CH{:}C{\cdot}CH_3$, obtained from propylene bromide by the action of alcoholic sodium hydroxide, was purified in a similar manner. It melts at $-110°$, at which temperature its vapour pressure = 10 mm.; it boils at $-23·5°$ under 760 mm., and its critical temperature is 129·5°. H. M. D.

Chlorination of *n*-Propyl Alcohol. GIUSEPPE ODDO and GUIDO CUSMANO (*Gazzetta*, 1905, **35**, i, 46—54).—The chlorination of *n*-propyl alcohol does not, as has been stated by Brochet (Abstr., 1896, i, 114), give rise only to $\alpha\beta$-dichloropropyl ether. The authors obtain a small quantity of this compound boiling at 97—100° under 15 mm. pressure and at 165—170° under the ordinary pressure, and find that on decomposition with sulphuric acid it yields β-chloropropaldehyde, which does not, however, undergo polymerisation (compare Brochet, *loc. cit.*).

From the fractions of the products of the reaction boiling either below or above 165—170° no definite compound could be obtained. The fraction boiling at 165—170° consists largely of a dichloropropyl ether, the pyridine compound of which yields, with platinic chloride, the derivative $(C_6H_{12}OCl_2,C_5H_5N)_2,PtCl_4$.

Brochet's interpretation of the mechanism of Wurtz and Frapolli's method for preparing chloroethyl ether by saturating a mixture of acetaldehyde and ethyl alcohol with hydrogen chloride (*Compt. rend.*, 1858, **47**, 418) is erroneous. T. H. P.

Normal C_9 Secondary Alcohols. LOUIS HENRY (*Bull. Acad. Roy. Belg.*, 1905, **7**, 19—22).—The author is engaged in investigating the influence on volatility of the displacement of various groups in these alcohols, which he proposes to synthesise by means of the action of alkyl magnesium haloids on appropriate aliphatic aldehydes.

T. A. H.

Hydrates of Acetol [Acetylcarbinol]. ANDRÉ KLING (*Compt. rend.*, 1905, **140**, 1040—1042).—Comparative measurements of the viscosity of mixtures of freshly distilled acetol and water have been made. When the dependence of the viscosity on the composition is represented graphically, a curve is obtained which exhibits a series of singular points. Well pronounced maximum points correspond with the hydrates $C_3H_6O_2,H_2O$ and $C_3H_6O_2,2H_2O$. Singular points are also found at compositions corresponding with $C_3H_6O_2,4H_2O$ and

$$2C_3H_6O_2,11H_2O.$$

The viscosity of acetol which has been kept for some time is greater than that of the freshly distilled product. The viscosity curves obtained for mixtures of this modified acetol with water are analogous but not identical with those furnished by the recently distilled substance. It is supposed that the change which takes place in the

acetol is one of condensation, for on distillation of a specimen which has been kept for a time a residue of higher boiling point is obtained (compare Abstr., 1903, i, 223). H. M. D.

Normal Diprimary Glycols. I. Tetramethylene Glycol. Jules Hamonet (*Bull. Soc. chim.*, 1905, [iii], 33, 513—525).—Most of the work recorded has been published already (Abstr., 1901, i, 187, 247, 251, and 305). Tetramethylene glycol may be readily characterised by means of its *phenylurethane*, which crystallises from boiling chloroform and melts at 180—181°. T. A. H.

Synthesis of Diprimary Substances, Higher Homologues of Trimethylene Derivatives, Ethers, Dihalogenated Derivatives, Glycols, &c., by the Action of Bromomethyl Ethers of Magnesium Derivatives of Bromo- (or Iodo-) Ethers of the Type $RO(CH_2)_nMgBr$. Jules Hamonet (*Bull. Soc. chim.*, 1905, [iii], 33, 525—528).—A *résumé* of work already published (Abstr., 1904, i, 401 and 467). T. A. H.

Syntheses in the Pentamethylene Series. Jules Hamonet (*Bull. Soc. chim.*, 1905, [iii], 33, 528—533).—A *résumé* of work already published (Abstr., 1904, i, 643 and 705). T. A. H.

Hexamethylene Glycol and its Derivatives. Jules Hamonet (*Bull. Soc. chim.*, 1905, [iii], 33, 533—541).—A *résumé* of work already published (Abstr., 1903, i, 251 and 306). T. A. H.

Oxidation of Octoglycol *iso*Butyrate. Karl Lesch and Anton Michel (*Monatsh.*, 1905, 26, 429—444. Compare Brauchbar and Kohn, Abstr., 1898, i, 353; Lederer, Abstr., 1901, i, 669; Kirchbaum, Abstr., 1904, i, 473).—The oxidation of octoglycol *iso*butyrate by potassium permanganate in sulphuric acid solution leads to the formation of three products depending on the concentration of the reaction mixture:

(*a*) A *substance*, $C_{11}H_{20}O_2$, which is a colourless oil, boils at 92° under 10 mm. pressure, forms an *additive* compound with 1 mol. of bromine in chloroform solution, and on hydrolysis yields *iso*butyric acid.

(*b*) A colourless, viscid *oil*, $C_{12}H_{22}O_4$, which distils at 170° under 17 mm. pressure and on hydrolysis yields *iso*butyric acid and the hydroxy-acid, $CHMe_2\cdot CH(OH)\cdot CMe_2\cdot CO_2H$.

(*c*) An acid, $C_{12}H_{22}O_5$, which forms compact, white crystals, melts at 79°, boils at 152° under 10 mm. pressure, and is probably identical with Brauchbar and Kohn's product boiling at 156—160°. These authors' supposed keto-ester boiling at 135° under 17 mm. pressure was probably unchanged octoglycol *iso*butyrate.

On hydrolysis with aqueous potassium hydroxide, the acid, $C_{12}H_{22}O_5$, yields *iso*butyric acid and a *lactone*, $C_8H_{14}O_3$, which crystallises in stellate aggregates, melts at 66—67°, sublimes when heated above its melting point, and forms a *calcium* salt, $C_8H_{14}O_4Ca$. The constitutions of the acid $C_{12}H_{22}O_5$ and of its product of hydrolysis are discussed. G. Y.

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Esterification of Glycerol. MARCEL P. S. GUÉDRAS (*Compt. rend.*, 1905, **140**, 1034).—The formation of glycerol monoacetin from glycerol and acetic acid takes place very rapidly at the ordinary temperature if casein is present. The casein appears to be unaltered by the change and seems to act as a catalytic agent. H. M. D.

The Oxidising Action of Impure Ether. HUGO DITZ (*Ber.*, 1905, **38**, 1409—1410. Compare Rossolimo, this vol., i, 295).—The author has previously pointed out (Abstr., 1901, ii, 222) that the blue solution of cobalt oxide in concentrated potassium hydroxide is only decolorised by ether when this contains peroxides. As this decolorisation by ether is quicker than that caused by hydrogen peroxide, it is inferred that the peroxides present in ether are more active than aqueous hydrogen peroxide. E. F. A.

Salts of Alkylsulphurous and Alkylsulphonic Acids. ARTHUR ROSENHEIM and WILLFRIED SAROW (*Ber.*, 1905, **38**, 1298—1305. Compare Abstr., 1898, i, 290).—Molecular weight determinations by the boiling point method show methyl, ethyl, and propyl sulphites to be unimolecular. *Propyl sulphite*, $SO(OPr^{\alpha})_2$, formed by the action of thionyl chloride on propyl alcohol, is a colourless liquid with an aromatic odour, which boils at 194°. When shaken intermittently for six months with 20 per cent. aqueous potassium hydroxide, ethyl sulphite is hydrolysed to an extent of only 80 per cent., yielding potassium sulphate and potassium ethanesulphonate. Under the same conditions, ethyl ethanesulphonate is completely hydrolysed in six hours to potassium ethanesulphonate.

Sodium propyl sulphite, $C_3H_7O_3SNa$, formed by the action of sulphur dioxide on a solution of sodium propoxide, crystallises in white leaflets and loses sulphur dioxide on exposure to the air. Similar unstable, crystalline salts are formed by the action of sulphur dioxide on organic bases in absolute alcoholic solution.

The action of methyl or ethyl sulphate on alkali alkyl sulphites suspended in absolute alcohol leads to the formation of the alkali sulphate, sulphur dioxide, and traces of the alkali alkylsulphonate. When heated with ethyl iodide in absolute alcohol at 120°, sodium ethyl sulphite yields Strecker's double salt of sodium ethanesulphonate, $(EtSO_2 \cdot ONa)_4NaI$ (*Annalen*, 1867, **148**, 190), which is formed also by the action of sodium iodide on ethyl ethanesulphonate in a sealed tube at 150°. The corresponding potassium double salt, $(EtSO_2 \cdot OK)_4,KI$, is formed by the action of potassium iodide on sodium ethyl sulphite, suspended in absolute alcohol, at 150—160°, or on ethyl ethanesulphonate at the laboratory temperature, or on ethyl sulphite at 150°. The double *salt*, $(EtSO_2 \cdot OK)_4,KBr$, is formed by shaking ethyl sulphite or ethyl ethanesulphonate with potassium bromide in absolute alcoholic solution. Strecker's double salt, $(EtSO_2 \cdot ONa)_4,NaCNS$ (*loc. cit.*), is formed similarly by the action of sodium thiocyanate on sodium ethyl sulphite. G. Y.

[Chloroacetic Acids.] JOHAN F. A. POOL (*Chem. Centr.*, 1905, i, 1005—1006. See this vol., ii, 425).

Chlorination of Fatty Acids. Hugo Blank (D.R.-P. 157816).—When sulphuryl chloride is added to a warmed mixture of a fatty acid with its chloride or anhydride, chlorination takes place readily, and is complete below the boiling point of the sulphuryl chloride, hydrogen chloride and sulphur dioxide being steadily evolved. The yield of monochloro-acid is quantitative, no secondary reactions taking place.

C. H. D.

Formation of Fatty Acids from Lactic Acid when Fused with Alkali Hydroxides. Henry S. Raper (*J. Physiol.*, 1905, **32**, 216—220).—When calcium lactate is fused with soda lime or potassium hydroxide and magnesium, a series of acids of the acetic series is formed (Hoppe-Seyler). In the present research, formic, acetic, propionic, butyric, and *iso*butyric acids were found; whether normal hexoic acid is also formed is doubtful. The non-volatile acids of high molecular weight are not higher fatty acids as stated by Hoppe-Seyler; they are heavier than water, are in part unsaturated, whilst their molecular weight is not far removed from that of hexoic acid. As *iso*butyric acid was found, Hoppe-Seyler's statement that the acids are normal is also incorrect. This mode of decomposition of lactic acid, moreover, does not explain the formation of fat from carbohydrates in the body.

W. D. H.

Use of Light Petroleum and Alcohol for the Separation of Oleic Acid from Stearic and other Solid Fatty Acids. K. W. Charitschkoff (*Chem. Rev. Fett. Harz. Ind.*, 1905, **12**, 106—109).—From the experiments described it is seen that by treating the mixed fatty acids of a fat or oil with light petroleum of sp. gr. 0·672 or alcohol of sp. gr. 0·886 at a temperature of 0°, the oleic acid is almost completely separated from the solid fatty acids. The fraction containing the latter had a melting point of 57° and iodine value of 43·3. The solubility of stearic acid was found to be 0·4 per cent. in light petroleum and 0·1 per cent. in alcohol. Alcohol separated the oleic acid more completely than the light petroleum, but the colouring substances were insoluble and remained in the stearic acid fraction. It is preferable, therefore, especially on a manufacturing scale, firstly to separate the oleic acid by means of alcohol, and then to remove the colouring substances from the stearic acid by treating the latter with a little light petroleum.

W. P. S.

New Acids of the Oleic Series. II. Δ^{α}-Hypogæic Acid. Giacomo Ponzio (*Atti R. Accad. Sci. Torino*, 1904—1905, **40**, 263—266. Compare Abstr., 1904, i, 548).—*α-Iodopalmitic acid*, $CH_3\cdot[CH_2]_{13}\cdot CHI\cdot CO_2H$, prepared by the action of potassium iodide on α-bromopalmitic acid in alcoholic solution, crystallises from light petroleum in shining plates, melts at 57°, is readily soluble in alcohol or chloroform, and remains unchanged under the influence of light.

Δ^{α}-Hypogæic acid, $CH_3\cdot[CH_2]_{12}\cdot CH\colon CH\cdot CO_2H$, obtained, together with a little α-hydroxypalmitic acid, by the action of alcoholic potass-

ium hydroxide solution on α-iodopalmitic acid, separates from alcohol in large, shining plates melting at 49° and resolidifying at 45°; it is stable in the air and is soluble in light petroleum and readily so in ether or chloroform. The *sodium* salt, $C_{16}H_{29}O_2Na$, is soluble in water and crystallises from alcohol in white prisms; the *calcium* salt (with $3H_2O$) dissolves to a slight extent in alcohol, but is insoluble in water; the *barium* salt is insoluble in water or alcohol. The *amide* crystallises from alcohol in prisms and is soluble in light petroleum, ether, or chloroform. The *dibromide* of the acid,

$$CH_3\cdot[CH_2]_{12}\cdot CHBr\cdot CHBr\cdot CO_2H,$$

crystallises from light petroleum in white prisms melting at 66° and is soluble in the ordinary organic solvents.

Neither Δ^{α}-hypogæic acid nor Δ^{α}-oleic acid (*loc. cit.*), when gently heated with dilute nitric acid and treated with sodium nitrite, undergoes change, whilst the hypogæic, oleic, and erucic acids, occurring in the vegetable kingdom, are transformed by this treatment into their isomerides, gaidic, elaidic, and brassidic acids. As oleic acid,

$$\begin{matrix}CH_3\cdot[CH_2]_7\\H\end{matrix}\!>\!C{:}C\!<\!\begin{matrix}H\\ [CH_2]_7\cdot CO_2H\end{matrix},$$

and erucic acid, $\begin{matrix}CH_3\cdot[CH_2]_7\\H\end{matrix}\!>\!C{:}C\!<\!\begin{matrix}H\\ [CH_2]_{11}\cdot CO_2H\end{matrix}$, have centro-symmetric configurations, whilst elaidic acid,

$$\begin{matrix}CH_3\cdot[CH_2]_7\\H\end{matrix}\!>\!C{:}C\!<\!\begin{matrix}[CH_2]_7\cdot CO_2H\\H\end{matrix},$$

and brassidic acid, $\begin{matrix}CH_3\cdot[CH_2]_7\\H\end{matrix}\!>\!C{:}C\!<\!\begin{matrix}[CH_2]_{11}\cdot CO_2H\\H\end{matrix}$, have plano-symmetric configurations, it may be assumed that Δ^{α}-hypogæic and Δ^{α}-oleic acids also have plano-symmetric structures, namely,

$$\begin{matrix}CH_3\cdot[CH_2]_{12}\\H\end{matrix}\!>\!C{:}C\!<\!\begin{matrix}CO_2H\\H\end{matrix} \quad\text{and}\quad \begin{matrix}CH_3\cdot[CH_2]_{14}\\H\end{matrix}\!>\!C{:}C\!<\!\begin{matrix}CO_2H\\H\end{matrix}$$

respectively, which is in agreement with their relatively high melting points. T. H. P.

Tetra-carbon Hydroxy-acids obtained by the Action of Hydrogen Cyanide on Epichlorohydrin, Epibromohydrin, and Epiethylin (Ethyl Glycide Ether). ROBERT LESPIEAU (*Bull. Soc. chim.*, 1905, [iii], 33, 460—469).—Most of the results recorded have already been published (Abstr., 1899, i, 243, 790; 1900, i, 425; 1903, i, 547, 684; 1904, i, 286, 471, and this vol., i, 9 and 255). When α-cyano-β-hydroxy-γ-ethoxypropane (this vol., i, 255) is treated with phosphoric oxide it yields *γ-ethoxycrotononitrile*, $OEt\cdot CH_2\cdot CH{:}CH\cdot CN$, which is liquid, boils at 190—191° under 750 mm. and at 82·5° under 17 mm. pressure. *Ethyl γ-ethoxycrotonate*, obtained by dehydrating ethyl β-hydroxy-γ-ethoxybutyrate (*ibid.*), boils at 201—203° under 760 mm. and at 95—96° under 19 mm. pressure and on hydrolysis with potassium hydroxide furnishes the corresponding *acid*. The latter is crystalline, melts at 45°, boils at 145—146° under 26 mm. pressure, and on oxidation with barium permanganate yields *ethylerythric acid*, $OEt\cdot CH_2\cdot CH(OH)\cdot CH(OH)\cdot CO_2H$, which crystallises from benzene, melts at 90—92°, and yields a gummy calcium salt.

T. A. H.

Semialdehyde of Maleic Acid. HERMANN FECHT (*Ber.*, 1905, 38, 1272—1274. Compare Limpricht, this Journal, 1873, 624; Baeyer, *Ber.*, 1877, 10, 1362; Hill and Allen, Abstr., 1897, i, 556).—An aqueous solution of bromine ($3\frac{1}{2}$ mols.) and potassium hydroxide (4 mols.) is added to a suspension of pyromucic acid (1 mol.) in water at 0°, the mixture, after remaining a day at the ordinary temperature, warmed to 30°, saturated with sodium sulphate, and extracted with ether, and the residue, obtained by evaporating the dry extract in a vacuum, distilled from the water-bath under 0·1—0·3 mm. pressure. The semialdehyde of maleic acid, $C_4H_4O_3$, obtained in this manner, crystallises from a mixture of benzene and ether in flat needles, melts at 55°, and boils with slight decomposition at 145° under 10 mm. pressure; in a thick layer, in concentrated aqueous or ethereal solution, or when fused, it is yellowish-green; it is easily soluble in water, alcohol, or ether, reduces ammoniacal silver or Fehling's solution, and colours rosaniline in sulphurous acid solution.

The *phenylhydrazone*, $C_{10}H_{10}O_2N_2$, crystallises in lemon-coloured needles and melts at 158—159°. The *oxime*, $C_4H_5O_3N$, forms a white, crystalline crust and detonates at 130—140°. The action of hydrogen chloride on the oxime in methyl-alcoholic solution leads to the formation of dimethyl fumarate.

When neutralised with sodium hydrogen carbonate and warmed with potassium cyanide in aqueous solution, maleic acid semialdehyde yields succinic acid. G. Y.

Formation of Salts in Solution, especially in the case of Substances exhibiting Tautomerism (Pseudo-acids, Pseudo-bases). III. JULIUS W. BRÜHL and HEINRICH SCHRÖDER (*Zeit. physikal. Chem.*, 1905, 51, 513—541. Compare Abstr., 1904, i, 646, 969; this vol., ii, 70, 235).—A rehearsal in the first place of the evidence in favour of the view that the esters of acetoacetic acid, their monoalkyl derivatives, and the esters of camphorcarboxylic acid are pure ketonic substances, without any traces of the enolic forms. Comparison of the spectrochemical functions shows that these substances are strictly homologous with the dialkyl derivatives of the esters of acetoacetic acid and the alkyl derivatives of the esters of camphorcarboxylic acid respectively. The latter compounds are undoubtedly ketonic, hence the former must also be ketonic. Further, the spectrochemical function for ethyl acetoacetate dissolved in water, methyl alcohol, or chloroform has the same value as for the pure ester, and a similar remark applies to methyl camphorcarboxylate dissolved in methyl alcohol or chloroform. Hence the forms in which the esters are present in these media are undoubtedly ketonic. The marked change of spectrochemical function when the esters are dissolved in a salt-forming medium, such as an alcoholic solution of sodium ethoxide, indicates that in these circumstances enolisation takes place immediately and can be easily detected.

These conclusions are not in harmony with some of Brühl's observations on the ferric chloride reaction (see Abstr., 1903, i, 314). The view is now adopted that ferric chloride is not a trustworthy reagent for the distinction of ketonic and enolic forms. As a salt, it is some-

what analogous to sodium ethoxide, and it may, like the latter, first induce enolisation when the medium permits, and only then give the characteristic reaction.

The paper contains a supplementary note, in which Brühl criticises Dimroth's recent work (this vol., i, 98) and emphasises the general applicability and trustworthiness of the optical method in settling problems of desmotropy. J. C. P.

Action of Hydroxylamine on Ethyl *iso*Nitrosoacetoacetate. ARTHUR HANTZSCH (*Ber.*, 1905, **38**, 1431).—A reply to Bouveault and Wahl (this vol., i, 257). J. J. S.

Ethyl Acetyl*iso*nitrosoacetoacetate. ANDRÉ WAHL (*Bull. Soc. Chim.*, 1905, [iii], **33**, 486—490).—In the preparation of ethyl diketobutyrate by the method already described (Abstr., 1904, i, 556, and next page), *ethyl acetyl*iso*nitrosoacetoacetate*,

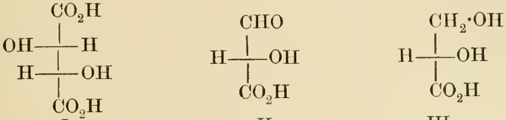
$COMe\cdot C(CO_2Et)\colon N\cdot OAc$,

is formed; this substance may also be obtained by the action of acetic anhydride on ethyl *iso*nitrosoacetoacetate. It is a viscid, slightly yellow liquid, which boils at 145° under 20 mm. pressure, and is heavier than, and insoluble in, water. Alkalis decompose it, forming a mixture of the cyanide, acetate, and carbonate of the alkali used. With hydroxylamine hydrochloride, ethyl dioximinobutyrate is produced. Phenylhydrazine reacts with ethyl acetyl*iso*nitrosoacetoacetate to form acetylphenylhydrazine and *ethyl α-acetyloximino-β-phenylhydrazinobutyrate*, $NHPh\cdot N\colon CMe\cdot C(CO_2Et)\colon N\cdot OAc$, which crystallises in yellow needles and melts at 123—124° and on treatment with potassium hydroxide in alcohol furnishes *ethyl α-oximino-β-phenylhydrazinobutyrate*, crystallising from alcohol in colourless spangles and melting at 165—166° when projected on the mercury bath. This ester may also be prepared by the action of phenylhydrazine on ethyl *iso*nitrosoacetoacetate dissolved in acetic acid, but in this case there is also formed Knorr's *iso*nitrosophenylmethylpyrazolone, due to loss of a molecule of ethyl alcohol (Abstr., 1887, 602). T. A. H.

Formation of Lævulic Acid and of Alcohol from Sugars. EMIL ERLENMEYER, jun. (*J. pr. Chem.*, 1905, [ii], **71**, 382—384).—Suggestions are made as to the intermediate substances formed in the production of lævulic acid by the action of hydrochloric acid on dextrose or lævulose, and of alcohol by fermentation. G. Y.

Glyceric Acid Derivatives. III. Configuration of Glyceric Acid. CARL NEUBERG and MARTIN SILBERMANN (*Zeit. physiol. Chem.*, 1905, **44**, 134—146. Compare Abstr., 1904, i, 220).—Details of the preparation of Will's hydroxypyruvic acid (aldehydoglyceric acid), $CHO\cdot CH(OH)\cdot CO_2H$ (Abstr., 1891, 542), from nitrocellulose are given. As solutions of the salts are lævorotatory, it cannot have the ketonic constitution suggested by Will. The most characteristic derivative is the *brucine* salt, $C_{29}H_{26}O_4N_2,C_3H_4O_3$, which crystallises from water in colourless needles. The acid readily reacts with potassium cyanide,

yielding a hydroxy-nitrile, which on hydrolysis yields *l*-tartaric acid. As the configuration of *l*-tartaric acid, I, is known to be



I. II. III.

the configuration II must necessarily represent that of the aldehydoglyceric acid molecule, and as this on reduction yields *l*-glyceric acid, configuration III must represent *l*-glyceric acid. The transformation of cellulose (a derivative of dextrose) into *l*-glyceric acid derivatives is analogous to the transformation of *d*-glycuronic acid into *l*-xylose (Abstr., 1903, i, 7), and of *d*-galactose into *l*-sorbose (Abstr., 1900, i, 208, 332). J. J. S.

Cineolic Acid. IV. Synthesis and Constitution of Cinenic Acid. HANS RUPE and PAUL SCHLOCHOFF (*Ber.*, 1905, **38**, 1502—1507. Compare Abstr., 1900, i, 371; 1901, i, 119, 578).—β-Hydroxy-β-methyl-ζ-heptanone, $OH{\cdot}CMe_2{\cdot}[CH_2]_3{\cdot}COMe$, prepared by the action of dilute sulphuric acid on methylheptenone, boils at 106° under 9 mm. and at 115—117° under 14 mm. pressure (compare Verley, Abstr., 1898, i, 557). When heated for 24 hours at 80° with anhydrous hydrogen cyanide, it forms *cinenonitrile*, which boils at 74·5° under 9 mm. pressure, water being eliminated from the nitrile initially formed, thus:

$$OH{\cdot}CMe_2{\cdot}C_3H_6{\cdot}CMe(OH){\cdot}CN = H_2O + CMe_2{<}\genfrac{}{}{0pt}{}{C_3H_6}{O}{>}CMe{\cdot}CN.$$

Cinenamide, $C_9H_{17}O_2N$, prepared by the action of alcoholic potassium hydroxide on the nitrile, separates from dilute alcohol in white needles and melts at 86—87°. When either the nitrile or the amide is hydrolysed by concentrated aqueous sodium hydroxide, cinenic acid is formed and is identical with the product previously described by Rupe and Ronus (*loc. cit.*).

Cinenic acid is represented by the formula

$$CMe_2{<}\genfrac{}{}{0pt}{}{C_3H_6}{O}{>}CMe{\cdot}CO_2H.$$

A. McK.

Preparation of αβ-Diketobutyric Esters. LOUIS BOUVEAULT and ANDRÉ WAHL (*Bull. Soc. chim.*, 1905, [iii], **33**, 475—481. Compare Sachs and Wolff, Abstr., 1903, i, 792, and Wieland and Bloch, *ibid.*, 1904, i, 596).—Many of the results recorded have already been published (Abstr., 1904, i, 556). Further details regarding the methods employed and some of the substances prepared are now given. Ethyl diketobutyrate hydrate, $COMe{\cdot}CO{\cdot}CO_2Et,\frac{1}{2}H_2O$ (*loc. cit.*), melts at 140° when projected on the mercury bath; *iso*butyl diketobutyrate hydrate, under the same conditions, melts at 115—120° (*loc. cit.*). *Methyl diketobutyrate*, prepared by the general method (*loc. cit.*), is a

pleasant-smelling, mobile, orange-yellow liquid, which boils at 65—68° under 12 mm. pressure; the *hydrate*, $COMe\cdot CO\cdot CO_2Me,H_2O$, crystallises from a mixture of ether and light petroleum and melts at 79—80°. T. A. H.

Reactions of Diketobutyric Esters. LOUIS BOUVEAULT and ANDRÉ WAHL (*Bull. Soc. chim.*, 1905, [iii], **33**, 481—486. Compare Abstr., 1904, i, 556 and 789, and preceding abstract).—The diketobutyric esters dissolved in acetic acid react with semicarbazide to form disemicarbazones, which are insoluble in most solvents and melt at comparatively high temperatures. *Methyl diketobutyratedisemicarbazone* melts at about 250°, and the *disemicarbazone* of the ethyl ester at about 270°.

With hydrazine in aqueous solution, the esters give rise to a *substance* which crystallises from acetic acid in ruby-red needles, melts above 300°, and dissolves in alkalis with an intensely violet colour. It is suggested that Knorr's rubazonic acid (Abstr., 1887, 602), which behaves similarly, may be a diphenyl derivative of this substance.

The diketobutyric esters combine with 2 mols. of aniline forming dianilides, which retain persistently 1 mol. of water and are therefore probably represented by one of the two formulæ

$$CMe(NHPh)_2\cdot CO\cdot CO_2R$$

or $COMe\cdot C(NHPh)_2\cdot CO_2R$. When these compounds are treated with phenylhydrazine, they are converted into phenylhydrazinophenylmethylpyrazolones.

Ethyl diketobutyrate dianilide, $C_{18}H_{18}O_2N_2,H_2O$, crystallises from alcohol in colourless needles and melts at 117—118°; the corresponding *derivatives* of the methyl and *iso*butyl esters are similar and melt at 115° and 114° respectively.

iso*Butyl diketobutyratephenylhydrazone* crystallises from a mixture of benzene and light petroleum in yellow, rhomboidal tablets and melts at 98°; the *phenylhydrazone* of the methyl ester is similar and melts at 98—99°. When boiled in acetic acid solution, both these phenylhydrazones yield Knorr's rubazonic acid (Abstr., 1887, 602), which indicates that they are β-phenylhydrazones (compare Abstr., 1904, i, 789). T. A. H.

Constitution of Certain Organic Salts of Nickel and Cobalt as they exist in Aqueous Solution. OLIN F. TOWER (*J. Amer. Chem. Soc.*, 1905, **27**, 386—391. Compare Abstr., 1903, ii, 134).—The investigations described in the earlier paper have been extended to the determination of the conductivity and freezing points of the nickel, cobalt, and magnesium glutarates, α-hydroxyglutarates, and trihydroxyglutarates.

It is found that the conductivity of these cobalt and nickel salts is somewhat greater than that of the corresponding malates and tartrates, but that the conductivity decreases as the number of hydroxyl groups increases, just as in the case of the succinic acid series.

These salts show but little tendency to polymerise, but the amount of polymerisation increases with the number of hydroxyl groups in the molecule. The tendency to undergo polymerisation shown by the cobalt and nickel malates and tartrates, however, does not appear to

increase in the case of the salts of the higher hydroxy-acids of this series. E. G.

α-Chloroglutaconaldehyde [β-Chloropenta-$\Delta^{\alpha\gamma}$-diën-α-ol-ε-al]. WALTER DIECKMANN (*Ber.*, 1905, **38**, 1650—1654. Compare Abstr., 1902, i, 786).—The author regards the compound described by Hantzsch as 3-chloro-1 : 2-diketo*cyclo*pentane (Abstr., 1889, 853) as the α-chloro-derivative of glutaconaldehyde, which has not been obtained in the free state, but which is the parent compound of the glutaconaldehyde dianilide obtained by Zincke (Abstr., 1904, i, 448 and 921 ; 1905, i, 241) and by Koenig (Abstr., 1904, i, 449). If this is so, the compound described by Ince (Abstr., 1890, 1090) as the dianilide of chlorodiketo*cyclo*pentane, being really a chloro-derivative of the glutaconaldehyde dianilide, must exhibit close analogy in properties with the latter. This is in reality the case, for Ince's dianilide exhibits in its salts the same tinctorial characteristics as are shown by Zincke and Koenig's dianilide. Further, the former is formed from 3-chloropyridine (by means of cyanogen bromide and aniline) and the latter from pyridine, and when boiled with hydrochloric acid the former is resolved into aniline and 3-chloro-1-phenylpyridinium chloride, which is perfectly analogous with phenylpyridinium chloride obtained in a similar way from Zincke and Koenig's dianilide.

3-*Chloro*-1-*phenylpyridinium chloride*, $CH{<}^{CCl:CH}_{CH-CH}{>}NPhCl$, is readily soluble in water or alcohol, and forms colourless crystals ; the *platinichloride*, $(C_{11}H_9NCl_2)_2PtCl_4$, crystallises from water in orange-red needles, melting and decomposing at 200—203°. T. H. P.

New Reactions and Derivatives of Glycuronic Acid. VII. CARL NEUBERG and WILHELM NEIMANN (*Zeit. physiol. Chem.*, 1905, **44**, 97—113).—The action of calcium hydroxide solution on glycuronic acid is similar to its action on dextrose (Kiliani, *Ber.*, 1882, **15**, 701 and 2957). When a 14 per cent. solution of glycuronic acid is left in contact with calcium hydroxide for several months, oxygen is absorbed and saccharone (Kiliani, Abstr., 1883, 962) and *l*-glyceric acid are formed :

$$CO_2H\cdot[CH(OH)]_4\cdot CHO \longrightarrow CO_2H\cdot[CH(OH)]_2\cdot CMe(OH)\cdot CO_2H + OH\cdot CH_2\cdot CH(OH)\cdot CO_2H.$$

Free glycuronic acid and solutions of its lactone do not react with hydrogen cyanide, even in the presence of a small amount of ammonia, but potassium cyanide and glycuronic acid react, forming a nitrile which, on hydrolysis, yields α-pentahydroxypimelic acid (Kiliani, Abstr., 1886, 936). Although the formation of two stereoisomeric acids is possible, only one has been isolated in the form of its calcium salt.

Carbamidoglycuronic acid (*ureidoglycuronic acid*),

$$NH_2\cdot CO\cdot N{:}CH\cdot[CH(OH)]_4\cdot CO_2H,$$

is formed when a solution of glycuronic anhydride and carbamide in 5 per cent. sulphuric acid is kept for $2\frac{1}{2}$ months at 40°. It is most readily isolated as the *barium* salt, $C_{14}H_{22}O_{14}N_4Ba$, which dissolves in

water, but is precipitated on the addition of absolute alcohol. The salt does not reduce, but when boiled for some time with Fehling's solution a precipitate of cuprous oxide is suddenly produced. It is lævorotatory, like all condensed glycuronic acid, and has $[\alpha]_D - 15{\cdot}83°$ at 17°. It is not hydrolysed by enzymes, such as kephir lactase, emulsin, or maltase. The free acid has only been obtained in aqueous solution. When this solution is concentrated, the acid is hydrolysed into its components. The addition of salts of heavy metals to solutions of the barium salt produces no precipitate.

Glycuronic acid osazone, $CO_2H{\cdot}[CH(OH)]_3{\cdot}C(:N_2HPh){\cdot}CH:N_2HPh$, may readily be obtained pure by Wohl and Neuberg's method (*Ber.*, 1900, **33**, 3108), using a temperature of 40°. It crystallises from 50 per cent. alcohol in long, felted needles, melts at 200—202°, and in most respects closely resembles glucosazone. It possesses acidic properties, and yields precipitates with baryta water or barium acetate solution.

The *osazone hydrazide*,

$$NHPh{\cdot}NH{\cdot}CO{\cdot}[CH(OH)]_3{\cdot}C(N_2HPh){\cdot}CH:N_2HPh,$$

is obtained when an alcoholic solution of the osazone is heated with phenylhydrazine at 150°. It crystallises in yellow, felted needles, changes colour at 210°, melts and decomposes at 212°, and is less readily soluble than the osazone. J. J. S.

Synthesis of Condensed Glycuronic Acids. VIII. CARL NEUBERG and WILHELM NEIMANN (*Zeit. physiol. Chem.*, 1905, **44**, 114—126).—The natural condensed glycuronic acids are usually represented as being closely related to the glucosides. Such constitutional formulæ have been confirmed by the synthesis of phenolglycuronic acid, euxanthic and *iso*euxanthic acids.

Diacetylbromoglycuronic lactone,

$$CHBr<\begin{matrix}CH(OAc){\cdot}CH\text{———}O \\ \quad\ | \\ O\text{———}CH{\cdot}CH(OAc)\end{matrix}>CO,$$

obtained by the action of acetyl bromide on glycuronolactone, crystallises in colourless needles, melts at 90° (corr.), dissolves readily in alcohol, ether, or ethyl acetate, is rapidly decomposed by water, and does not reduce cold Fehling's solution. When condensed with potassium methoxide and euxanthone in methyl-alcoholic solution, it yields an acid identical with natural euxanthic acid and an isomeric acid, iso*euxanthic acid*, $C_{19}H_{16}O_{10}$, which melts at 157—159°. Its rotatory power is less than that of euxanthic acid, $[\alpha]_D - 87{\cdot}4°$.

The following constitutional formula is suggested for euxanthic acid:

$$OH{\cdot}C_6H_3<\begin{matrix}C(OH)_2\\O\end{matrix}>C_6H_3{\cdot}O{\cdot}CH<\begin{matrix}[CH(OH)]_2\\O\end{matrix}>CH{\cdot}CH(OH){\cdot}CO_2H,$$

and a similar formula, less H_2O, for the *iso*-acid, the OH group probably occupying different positions in the two acids.

Phenolglycuronic acid,

$$OPh{\cdot}CH<\begin{matrix}[CH(OH)]_2\\O\end{matrix}>CH{\cdot}CH(OH){\cdot}CO_2H,$$

crystallises from water in long, prismatic needles when free from glycuronic acid, melts at 150—151°, has $[\alpha]_D^{17°} - 83{\cdot}3°$, is readily soluble

in alcohol and hot ethyl acetate, and yields soluble salts. It is probably identical with the substance described by Kütz (Abstr., 1890, 1286).

J. J. S.

Action of Ethyl Oxalic Chloride on Ethyl Sodiomalonate. HERBERT KURREIN (*Monatsh.*, 1905, **26**, 373—378).—The action of ethyl oxalic chloride on ethyl sodiomalonate in benzene solution leads to the formation of *ethyl ketoethanetricarboxylate*,

$$CO_2Et{\cdot}CO{\cdot}CH(CO_2Et)_2,$$

which is a colourless oil; it boils at 86° under 12 mm. pressure, and is hydrolysed by boiling alcoholic potassium hydroxide. The *acid*, $C_5H_4O_7,2H_2O$, melts at 99°, loses carbon dioxide at 120—130°, and forms an anhydrous *calcium* salt, $(C_5H_4O_7)_2Ca_3$.

G. Y.

Action of Hydrogen Chloride on Mixtures of Nitriles and Aldehydes or Ketones. FRANZ HENLE and GUSTAV SCHUPP (*Ber.*, 1905, **38**, 1369—1371).—When acetonitrile is mixed with either acetaldehyde, benzaldehyde, acetone, or acetophenone, and hydrogen chloride passed into the mixture, a small quantity of acetamide hydrochloride is obtained; with acetone, propionitrile gives propionamide hydrochloride under similar conditions. On passing hydrogen chloride into a mixture of benzonitrile and acetaldehyde, ethylidenedibenzamide, $CHMe(NHBz)_2$, is formed; benzyl cyanide and acetaldehyde, under similar conditions, give ethylidenediphenylacetamide,

$$CHMe(NH{\cdot}CO{\cdot}CH_2Ph)_2;$$

benzyl cyanide and acetone give phenylacetamide. Benzonitrile and benzyl cyanide are not changed by benzaldehyde or acetophenone in presence of hydrogen chloride.

W. A. D.

Preparation of Mesoxaldialdehyde. FRANZ HENLE and GUSTAV SCHUPP (*Ber.*, 1905, **38**, 1372—1373).—On passing nitrous vapours into an ice-cold aqueous suspension of di*iso*nitrosoacetone, nitrous oxide is evolved, and a solution containing mesoxaldehyde, $CO(CHO)_2$, is obtained; that about 30 per cent. of this substance is formed is shown by the production of mesoxaldialdehydebisphenylhydrazone on adding phenylhydrazine acetate and sodium acetate to the cold solution.

When nitrous acid is passed into a suspension of di*iso*nitrosoacetone in ether, garnet-red crystals separate, which effloresce and become yellow in the air and explode when heated; on adding cold dilute solutions of sodium or barium hydroxide, ammonia, potassium cyanide, or sodium acetate to this substance, an explosion, accompanied by a large yellow flame, occurs. The behaviour of the substance resembles that of nitroamide.

W. A. D.

Methylglyoxal and Mesoxaldialdehyde. CARL D. HARRIES and HANS TÜRK (*Ber.*, 1905, **38**, 1630—1636. Compare Abstr., 1903, i, 605).—*Mesityl oxide ozonide*, $C_6H_{10}O_5$, is obtained as a very explosive, viscous green syrup. When gently heated in solution, it gives acetone peroxide, $CMe_2{<}\begin{smallmatrix}O\\|\\O\end{smallmatrix}$, and the di-polymeride of *methylglyoxal*,

$$(CHO{\cdot}COMe)_2,$$

which forms a hygroscopic, glassy mass. *Methylglyoxal semicarbazone*, $C_5H_{10}O_2N_6$, dissolves slightly in water, from which it separates in crystals melting at about 257°. *Methylglyoxal monoacetal*,

$CH_3 \cdot CO \cdot CH(OEt)_2$,

prepared by the action on methylglyoxal of absolute alcohol containing 2 per cent. of hydrogen chloride, is obtained as a highly refractive liquid boiling at 30° under 10 mm. pressure.

Phorone diozonide, $C_9H_{14}O_7$, is obtained as an explosive, pale green, viscous syrup which ignites if left in the air. It is gradually decomposed by ice-water, yielding acetone peroxide and a *hydrate* of mesoxaldialdehyde, $C_3H_4O_4$, which is a clear, viscous syrup. Anhydrous *mesoxaldialdehyde*, $CHO \cdot CO \cdot CHO$, forms a pale yellow, brittle mass which is extremely hygroscopic. The melting point of the triphenylhydrazone prepared by the authors is 156°, whereas von Pechmann and Jenisch gave 166° (Abstr., 1892, 161). T. H. P.

Chemical Action of Light. IX. GIACOMO L. CIAMICIAN and PAUL G. SILBER (*Ber.*, 1905, **38**, 1671—1675. Compare this vol., i, 335).—A mixture of acetone and aqueous 3·3 per cent. hydrogen cyanide, exposed to sunlight for several months, gave rise to the following products: ammonium oxalate, acetonylcarbamide, α-hydroxy*iso*butyramide, α-amino*iso*butyric acid. In the dark, the sole product formed was acetone cyanohydrin. Similarly, aldehyde-ammonia and aqueous 3·3 per cent. hydrogen cyanide, after six months' exposure to sunlight, gave rise to a yellowish-brown, gummy product, from which a *compound*, $C_6H_{12}O_3N_2$, isomeric with alanylalanine, was obtained. This crystallises in thick, colourless plates melting at 232°, and probably has the constitution $CO_2H \cdot CHMe \cdot NH \cdot CHMe \cdot CO \cdot NH_2$.

E. F. A.

Methylheptenone Oxides. HANS RUPE and PAUL SCHLOCHOFF (*Ber.*, 1905, **38**, 1498—1502).—Methylheptenol, prepared by the reduction of methylheptenone by sodium, boils at 74—75° under 10 mm. pressure. When agitated for 16—20 hours with dilute sulphuric acid, it is converted into the glycol, *β-methylheptane-βζ-diol*, $OH \cdot CMe_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot OH$, a viscid oil, which boils at 122—123° under 13 mm. pressure and, when distilled with sulphuric acid in a current of steam, gives cinene, boiling at 127—128° (Wallach gives 127—129°). Cinene yields white needles or prisms of an *additive compound* with hydrogen bromide in acetic acid solution, which is stable only in presence of an excess of hydrogen bromide and undergoes immediate decomposition in air.

Dimethylheptenol, prepared by the action of magnesium methyl iodide on methylheptenone, boils at 76—78° under 12 mm. pressure (Barbier gives 79° under 12 mm. pressure). By the action of sulphuric acid, it is converted into the glycol, *βζ-dimethylheptane-βζ-diol*, $OH \cdot CMe_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CMe_2 \cdot OH$, which separates from ether in glassy crystals and melts at 62°; the *diacetyl* derivative is a viscid oil, which boils at 135·5—136° under 14 mm. pressure. When the glycol is added to an ice-cold solution of 70 per cent. sulphuric acid, it is

dehydrated, *methylcinene*, $CH_2<\begin{smallmatrix}CH_2\cdot CMe_2\\CH_2\cdot CMe_2\end{smallmatrix}>O$, being formed as an oil boiling at 142—142·5° under 744 mm. pressure. By the action of a mixture of glacial acetic acid and hydrogen bromide, it is converted into an additive *compound*, $C_9H_{19}OBr$, crystallising in needles and melting at 63—64°; the latter compound is instantaneously decomposed by water. Methylcinene forms an additive compound with hydroferricyanic acid. A. McK.

Preparation of β-Methylglucoside. Léon Maquenne (*Bull. Soc. chim.*, 1905, [iii], **33**, 469—471).—Dextrose is dissolved in water and methyl sulphate is added together with enough potassium hydroxide solution of sp. gr. 1·4 to render the liquid alkaline until the end of the reaction, when it should be almost neutral. After 30 minutes, the mixture is concentrated, poured into excess of alcohol, and the filtrate evaporated to a syrup and set aside to crystallise. After recrystallisation twice from warm alcohol, a yield of β-methylglucoside equivalent to 20 per cent. of the weight of dextrose employed is obtained. A further quantity may be secured by re-treatment of the residues with methyl sulphate and potassium hydroxide. The glucoside softens at 96° and loses a $\frac{1}{2}$ mol. of water and then melts at about 108°. No α-methylglucoside is formed by this method. T. A. H.

Action of Inorganic Compounds on Optically Active Polyhydric Alcohols and Acids. Hermann Grossmann (*Ber.*, 1905, **38**, 1711—1719. Compare Rimbach and Weber, following abstract).—A solution of lead acetate in presence of sodium hydroxide produces a considerable increase in the molecular rotation of dextrose solutions. The increased rotation is observed immediately after mixing and it shows a tendency to fall again after a short time. Lead acetate solution itself produces but little effect; this increases with the time (Lobry de Bruyn and Alberda van Ekenstein, Abstr., 1896, i, 116 and 588). The effect of an alkaline lead acetate solution on lævulose is to diminish the lævorotation and ultimately to induce dextrorotation; this reaches its maximum, $[\alpha]_D + 66·7°$ at 17°, when the ratio of lævulose to lead acetate molecules is 2 : 3. If the concentration of the acetate is increased, the dextrorotation decreases and ultimately changes sign again.

A solution of invert sugar in the presence of alkaline lead acetate changes from lævo- to dextro-rotatory, reaches a maximum, and then diminishes with increasing lead acetate concentration.

Mannitol in the presence of neutral bismuth nitrate (molecular proportions) exhibits a dextrorotation which increases with dilution. No multirotation is shown on keeping, although some change goes on in the solution. In the presence of alkali, bismuth nitrate produces a still more marked effect on the rotation of mannitol.

Rosenheim and Schütte's ammonium titanotartrate (Abstr., 1901, ii, 246) is lævorotatory in concentrated solution, but on dilution becomes strongly dextrorotatory. For $c = 2·317$, $[\alpha]_D$ is $-40·1°$, and for $c = 0·1448$ $[\alpha]_D$ is $+276·3°$ at 20°. J. J. S.

Action of Inorganic Substances on the Rotation of Lævulose and Dextrose. EBERHARD RIMBACH and O. WEBER (*Zeit. physikal. Chem.*, 1905, **51**, 473—493. Compare Rimbach and Schneider, Abstr., 1903, ii, 624).—The chlorides of the alkaline earth metals have little effect on the rotation of dextrose, but raise the rotation of lævulose to an extent which increases with their concentration. The relative effect of zinc, cadmium, and mercury salts is similar. The influence of free boric acid on the rotation of lævulose and dextrose is practically nil, but the conductivity of the solutions containing both sugar and acid is higher than that of the solutions containing the acid alone—a contrast to the usual effect of the sugars, which is to diminish the conductivity of the inorganic substance. Borax reduces very markedly the rotation of both lævulose and dextrose. Cerium and thorium salts have a very slight effect on the rotation of dextrose, but increase that of lævulose to a notable extent. Zirconium oxychloride reduces the rotation of both sugars very markedly, the effect being greatest in the case of dextrose. The final value of the rotation, however, is reached only after some time, and the sugar solutions containing larger quantities of zirconium gradually assume an intense reddish-brown colour. When a solution of lævulose or dextrose containing zirconium salt is warmed, a green fluorescence is observed—a behaviour exhibited also by several other sugars. Arsenious acid raises slightly the rotation of lævulose, but is without effect on that of dextrose. The influence of compounds of molybdenum, tungsten, and uranium is varied and of no very definite character.

The effect of borax, referred to above, is probably due, to a certain extent at least, to the presence of hydroxyl ions produced by hydrolysis. This leads the authors to study quantitatively the action of hydroxyl ions (from sodium hydroxide, triethylamine, and sodium carbonate) on dextrose. It is found that the reaction, as followed by the change of rotation, is one of the second order. When the other conditions are fixed, the velocity is proportional to the concentration of the hydroxyl ions. J. C. P.

Nature of Iodide of Starch. MAURICE PADOA and B. SAVARÈ (*Atti R. Accad. Lincei*, 1905, [v], **14**, i, 467—476).—The authors show, by conductivity measurements, that iodide of starch must be regarded as an additive product of iodine, starch, and potassium iodide (or hydrogen iodide), the molecular ratio between the iodine and starch ($C_6H_{10}O_5$) being 4. It was not found possible to obtain a constant relation between the iodine and hydriodic acid. The existence is proved of only one additive product, the modifications of the colour being probably caused by physical modifications of the particles of the iodide of starch. The latter forms solutions of the nature of suspensions. T. H. P.

Preparation of Betaine Salts from Molasses. CARL STIEPEL (D.R.-P. 157173. Compare Staněk, Abstr., 1902, i, 427).—In the extraction of betaine from molasses and similar products, the employment of chemical reagents to break up the complex compounds present has hitherto been considered necessary. It is now

found that the betaine may be extracted by simple agitation with 95 per cent. alcohol. The alcoholic solution is decolorised by charcoal and evaporated to a syrup. It may be again dissolved in alcohol and the betaine hydrochloride precipitated by the addition of concentrated hydrochloric acid or gaseous hydrogen chloride.

C. H. D.

Electrolysis of Glycine. OTTO KÜHLING (*Ber.*, 1905, **38**, 1638—1646).—Aqueous glycine solutions are at first very bad conductors, but as the electrolysis proceeds the conductivity of the solutions increases owing to the formation of better conducting products.

After electrolysis, the solutions are found to contain ammonia and small quantities of ethylenediamine, whilst if the conductivity of the original solution is increased by the addition of an indifferent substance, no ethylenediamine is obtained. The gaseous products consist almost entirely of carbon dioxide, whilst carbon monoxide, nitrogen, and formic acid are formed in small quantities.

The resolution of glycine by electrolysis probably takes place in two ways: (1) Giving NH_3 and $CH_2{\cdot}CO_2'$ and (2) giving $\cdot NH_3{\cdot}CH_2\cdot$ and CO_2'.

T. H. P.

Ethyl Diaminosuccinate. JULIUS TAFEL and HERMANN STERN (*Ber.*, 1905, **38**, 1589—1592. Compare Tafel, Abstr., 1887, 468; Farchy and Tafel, Abstr., 1893, i, 692).—*Ethyl μ-diaminosuccinate*, $C_8H_{16}O_4N_2$, obtained from its hydrochloride by Curtius' method, crystallises in long needles, melts at 38°, distils at 160—166° under 15 mm. pressure, has an alkaline reaction in aqueous solution, gives a blue coloration with copper sulphate, and forms a picrate melting at 121°. The *diacetyl* derivative, $C_{12}H_{20}O_6N_2$, crystallises in plates and melts at 180·5°; the *dibenzylidene* derivative crystallises in needles, melts at 144·5°, and is hydrolysed by cold 10 per cent. hydrochloric acid; the *condensation* product with ethyl acetoacetate, $C_{20}H_{32}O_8N_2$, crystallises in prismatic needles and melts at 77°; the *condensation* product with acetylacetone, $C_{18}H_{28}O_6N_2$, crystallises in prismatic needles and melts at 138—139°.

G. Y.

α-Amino-derivatives of Adipic Acid, β-Methyladipic Acid, and Pimelic Acid. WALTHER DIECKMANN (*Ber.*, 1905, **38**, 1654—1661).—*α-Aminoadipic acid* (Sörensen, Abstr., 1903, i, 833), $CO_2H{\cdot}CH(NH_2){\cdot}[CH_2]_3{\cdot}CO_2H$, prepared by the reduction of α-hydroxyaminoadipic acid with tin and hydrochloric acid, crystallises in colourless, microscopic plates, which melt and decompose at 205—206° and give a reddish-brown coloration with ferric chloride; the *copper* salt (with $2H_2O$) separates as a deep blue, crystalline precipitate.

2-Piperidone-6-carboxylic acid, $C_5NH_8O{\cdot}CO_2H$, formed on heating α-aminoadipic acid at its melting point, crystallises from water in transparent, pointed prisms, melting at 177—178°, and forms crystalline *copper*, *barium*, and *silver* salts.

δ-Amino-β-methyladipic acid,

$$CO_2H{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2H,$$

was isolated in the form of a very sparingly soluble *copper* salt crystallising with $2H_2O$. *a-Benzamino-γ-methyladipic acid* crystallises in colourless needles melting at 172—173°. 4-*Methyl*-2-*piperidone*-6-*carboxylic acid*, $CHMe<\begin{matrix}CH_2\cdot CH(CO_2H) \\ CH_2\text{———}CO\end{matrix}>NH$, crystallises in well-formed, transparent prisms melting at 124°, and forms a green, crystalline *copper* salt; the *silver* salt separates in colourless needles.

a-Aminopimelic acid, $CO_2H\cdot CH(NH_2)\cdot[CH_2]_4\cdot CO_2H$, forms colourless, microscopic plates melting and decomposing at 225°; the bright blue *copper* salt is sparingly soluble. E. F. A.

Synthesis of Aminohydroxysuccinic Acid. CARL NEUBERG and MARTIN SILBERMANN (*Zeit. physiol. Chem.*, 1905, **44**, 147—156. Compare Abstr., 1904, i, 220).—Aminohydroxy-acids may be obtained from diamino-acids by means of nitrous acid. Care must be taken that only the theoretical amount of nitrous acid is employed; this may be accomplished by using silver nitrite and the hydrobromide of the base or barium nitrite and the sulphate of the base (Witt and Ludwig, Abstr., 1904, ii, 124, 171).

Aminohydroxysuccinic acid has been obtained by the action of barium nitrite on a solution of Lehrfeld's diaminosuccinic acid (Abstr., 1882, 163) in sulphuric acid solution, and was isolated as its *cupric* salt, $C_4H_5O_5NCu$. The acid melts at 314—318° and has the meso-configuration as it is derived from *s*-dibromosuccinic acid, which can readily be transformed into meso-tartaric acid.

The aminohydroxy-acid described by Skraup (Abstr., 1904, i, 539) is probably the optically active or partially racemised acid.

J. J. S.

The Formation of Mercury Fulminate. LOTHAR WÖHLER and K. THEODOROVITS (*Ber.*, 1905, **38**, 1345—1351).—As stated by Stahlschmidt (*Ann. Phys. Chem.*, 1860, **20**, 547), mercury fulminate may be prepared by the action of mercuric nitrate and nitric acid on the so-called "lignone," obtained by the dry distillation of wood; but the presence of nitrous fumes in the nitric acid used is essential for a successful result. Both methylal and acetal, preferably the latter, also yield mercury fulminate when treated in the same way as alcohol in the ordinary method. It is doubtful whether purified lignone is identical with methylal, as supposed by Dancer (*Annalen*, 1864, **132**, 240), as under certain conditions it behaves in the interaction differently from this substance. Acetaldehyde and its polymerides, paraldehyde and metaldehyde, readily yield pure mercury fulminate, but even in the most favourable circumstances, as in the case of alcohol, there is considerable waste of material. Methyl alcohol, formaldehyde, trioxymethylene, and formic acid do not give rise to mercury fulminate under any conditions; the same is true of substances containing three or more carbon atoms, such as propyl and *iso*propyl alcohols, allyl alcohol, propaldehyde, *iso*butaldehyde, acetone, and methyl ethyl ketone. Oximes, for example, acetaldoxime, do not generate mercury fulminate.

It thus appears that a chain of two carbon atoms is necessary for the formation of mercury fulminate; as the latter is not formed from

ethylene glycol, glyoxal, glyoxime, or acetonitrile, the following structures appear to be essential: $\cdot CH_2 \cdot OH$, $\cdot CH{<}^{O\cdot}_{O\cdot}$, $\cdot CHO$, or $\dot{:}CH \cdot O \cdot$.

W. A. D.

Molecular Weight of Fulminic Acid. LOTHAR WÖHLER (*Ber.*, 1905, **38**, 1351—1359).—The only real evidence in favour of the unimolecular formula for fulminic acid appears to be the three syntheses of fulminates by Nef (Abstr., 1895, i, 3), Jones (Abstr., 1898, i, 172), and Biddle (Abstr., 1900, i, 137); of these syntheses, the author could only successfully repeat that due to Nef.

Anhydrous sodium fulminate can be prepared in theoretical yield by the action of sodium amalgam on mercury fulminate suspended in absolute alcohol; it differs from the hydrated salt (Ehrenberg, Abstr., 1885, 1191), which is obtained pure only with great difficulty, in being quite stable at 100°. Measurements of its molecular weight in aqueous solution, taking into account the degree of dissociation, agree absolutely with the assumption of the formula CNOH for fulminic acid; the same view is supported by the difference, at 0°, of the equivalent conductivities of solutions of the salt at concentrations $N/32$ and $N/1024$.

The fact that a chain of two carbon atoms is necessary in the synthesis of mercury fulminate (preceding abstract) seemed to point to Steiner's bimolecular formula, $C_2H_2O_2N_2$, for fulminic acid being correct. It is, however, possible that the nitrous acid necessary in the production of mercury fulminate may give rise primarily to a nitrosyl derivative susceptible of easy decomposition. But an attempt, made from this standpoint, to prepare mercury fulminate by the action of mercury or its nitrate and nitric acid on ethyl nitroacetate was unsuccessful.

W. A. D.

Condensation Products from Glycoluril and Formaldehyde. ROBERT BEHREND, EBERHARD MEYER, and FRANZ RUSCHE (*Annalen*, 1905, **339**, 1—37).—In the preparation of glycoluril from glyoxal and carbamide, by-products are produced, especially when too small a quantity of carbamide is used: the *compound* $C_{11}H_{18}O_{10}N_6,H_2O$, formed from carbamide (3 mols.) and glyoxal (4 mols.), is an amorphous, brownish-yellow substance; the *compound* $C_{20}H_{36}O_{19}N_{12}$, from carbamide (6 mols.) and glyoxal (7 mols.), is a brownish-yellow powder; both substances are soluble in alkali hydroxides.

When heated with formaldehyde in solution in hydrochloric acid, glycoluril condenses to form two compounds according to the quantity of formaldehyde used. The *compound* $C_{16}H_{18}O_6N_{12}$, formed from 3 mols. of glycoluril and 4 mols. of formaldehyde, is a white powder; it is converted by further treatment with formaldehyde into the *compound* $C_{18}H_{18}O_6N_{12}$, which is also formed directly from 3 mols. of formaldehyde and 1 mol. of glycoluril. The substance first mentioned is decomposed by warming with concentrated sulphuric acid, yielding the compound $C_{10}H_{11}O_4N_7,2H_2O$, which crystallises in needles, losing water at 100°. This compound is exceedingly stable and forms a series of additive compounds with inorganic salts. With potassium

permanganate, it yields a *substance* crystallising in red or violet rods, with potassium bromide the *compound* $3C_{10}H_{15}O_6N_7,2KBr,5H_2O$, crystallising in colourless rods, with ammonium chloride the *compound* $3C_{10}H_{15}O_6N_7,2NH_4Cl,10H_2O$, forming regular crystals, with silver nitrate the *compound* $3C_{10}H_{15}O_6N_7,AgNO_3,6H_2O$, crystallising in six-sided prisms, with chromic acid the *compound* $C_{10}H_{15}O_6N_7,H_2CrO_4,H_2O$, forming ruby-red crystals, with potassium chromate the *compound* $2C_{10}H_{15}O_6N_7,K_2CrO_4,5H_2O$, forming straw-yellow crystals, with potassium dichromate the *compound*

$$5C_{10}H_{15}O_6N_7,2K_2Cr_2O_7,$$

crystallising in orange-red needles, with potassium ferrocyanide the *compound* $7C_{10}H_{15}O_6N_7,2K_4Fe(CN)_6,10H_2O$, crystallising in white needles, with potassium ferricyanide the *compound*

$$7C_{10}H_{15}O_6N_7,2K_3Fe(CN)_6,$$

crystallising in yellow rods, with platinic chloride the *compound* $7C_{10}H_{15}O_6N_7,2H_2PtCl_6,20H_2O$, crystallising in yellow prisms, and with sodium aurichloride the *compound* $C_{10}H_{15}O_6N_7,NaAuCl_4,5H_2O$, forming golden-yellow crystals. Many organic dyes yield coloured precipitates with this compound.

Glycoluril does not condense with carbamide in alkaline solution, but the glycoluril is obtained from the mixture in the form of leaflets, and not in the usual needles or octahedra. K. J. P. O.

Condensation of *iso*Dialuric Acid with Thiocarbamide. Richard Bartling (*Annalen*, 1905, **339**, 37—40. Compare Abstr., 1901, i, 262).—By oxidation with nitric acid of the condensation product from *iso*dialuric acid and thiocarbamide, Vogel (*loc. cit.*) has obtained a compound which was thought to be identical with dilituric acid. A more extended investigation has confirmed this supposition. It appears, however, that the compound produced is not the free acid, but the ammonium salt, $C_4H_6O_5N_4$; the salt is not decomposed by nitric acid. The identity of this salt with ammonium diliturate, prepared by other methods, was shown by crystallographic measurements and by the solubility in water. Characteristic ferrous and barium salts were also obtained. K. J. P. O.

Cyanogen Bromide and Hydroxylamine. II. Heinrich Wieland (*Ber.*, 1905, **38**, 1445—1461. Compare Abstr., 1904, i, 628). —The reaction between cyanogen bromide and free hydroxylamine in alcoholic ethereal solution at the ordinary temperature is violent and almost explosive; it proceeds mainly according to the equation $2CNBr + 2NH_2{\cdot}OH = HCN + N_2 + CO_2 + NH_4Br + HBr$. The reaction is largely modified by working at $-20°$ with the compounds dissolved in a mixture of methyl alcohol and ether free from water, when a 75 per cent. yield of *dihydroxyguanidine hydrobromide*,

$$OH{\cdot}NH{\cdot}C(:NH){\cdot}NH{\cdot}OH,HBr,$$

may be obtained. It is probably formed as follows: $CNBr + NH_2{\cdot}OH = CN{\cdot}NH{\cdot}OH + HBr$; $OH{\cdot}NH{\cdot}CN + NH_2{\cdot}OH,HBr = OH{\cdot}NH{\cdot}C(:NH){\cdot}NH{\cdot}OH,HBr$, and may be freed from ammonium bromide by solution in methyl alcohol and ether. It crystallises in

colourlesss, flat, hygroscopic needles, decomposes slowly at about 95°, rapidly at 120°, and is insoluble in benzene, ether, or chloroform. It is stable in the presence of acids and possesses strong reducing properties. With ferric chloride, its solutions give a bluish-black coloration, rapidly changing to green. When reduced with aluminium amalgam, it yields methylamine; with stannous chloride, ammonia. The blood-red alkaline solution changes to orange, and from this solution the following compounds have been isolated: azoxydicarbonamide dioxime, ammonium di*iso*nitrosotetrahydrotetrazine, and hydrazodicarbonamide.

Azoxydicarbonamide dioxime,

$$OH\cdot N\!:\!C(NH_2)\cdot NO\!:\!N\cdot C(NH_2)\!:\!N\cdot OH,$$

is precipitated when the alkaline mixture is carefully treated with nitric acid. It crystallises from water at 60° as an orange-red powder, decomposing at 99°, is insoluble in organic solvents, and dissolves in hot water, but slowly decomposes. It gives a brownish-violet coloration with ferric chloride and does not show Thiele's azo-reaction (Abstr., 1892, 1429). As a base, it dissolves in acids, but the solutions immediately undergo decomposition. The *silver*, *lead*, and *mercuric* salts have been obtained as dark precipitates. On reduction with hydrogen sulphide, the azoxy-compound yields a readily soluble, colourless *hydrazo*-compound melting and decomposing at 190°.

*Ammonium di*iso*nitrosotetrahydrotetrazine*,

$$OH\cdot N\!:\!C{<}\begin{matrix}N=\!=\!=N\\ NH\cdot NH\end{matrix}{>}C\!:\!N\cdot ONH_4,$$

is found in the filtrate from the azoxy-compound, and may also be obtained by the action of ammonia or sodium hydrogen carbonate on the salts of dihydroxyguanidine. It forms feathery, carmine-red crystals which explode at 158°; when acidified, a yellow solution of the free hydroxyl compound is obtained, but so far this has not been isolated. When warmed with acids, nitrous acid is formed, and this probably accounts for the fact that the compound gives Thiele's azo-reaction. Coloured precipitates of *silver*, *copper*, and *mercuric* derivatives have been obtained.

Hydrazodicarbonamide (Thiele, Abstr., 1892, 1298, 1429) usually accompanies the ammonium salt described above and is most readily obtained, together with potassium cyanate, by the action of alcoholic potassium hydroxide on dihydroxyguanidine.

Aminomethylnitrosolic acid, $NO\cdot C(NH_2)\!:\!N\cdot OH$, obtained by the reaction of cyanogen bromide, hydroxylamine, and alcoholic potassium hydroxide, better by the action of methyl-alcoholic potash on dihydroxyguanidine hydrobromide or by the oxidation of the hydrobromide, crystallises from pure ether in large, flat, green plates, which decompose with violence at 38°. The *potassium* salt, $CH_2O_2N_3K$, crystallises from 80 per cent. alcohol in brilliant, steel-blue needles, which decompose at 213° or explode at 220°. It is not decomposed by dilute alkalis, but concentrated alkalis yield ammonia and hydrocyanic and carbonic acids. The *silver*, *copper*, *zinc*, and *ammonium* salts have been prepared and also a complex *mercuric* salt. The acid liberates iodine from acidified potassium iodide and sulphur from hydrogen sulphide, and like Piloty and von Schwerin's nitroso-compounds (Abstr., 1901, i, 516) may be used in place of nitrous acid for diazotising.

The *benzoate*, NO·C(NH$_2$):N·O·COPh, forms glistening, green plates, which melt and decompose at 119°. J. J. S.

Action of Oxalic Acid on Lead Ferrocyanide. AUGUSTE LEUBA (*Ann. Chim. anal.*, 1905, **10**, 143—145).—When lead ferrocyanide is boiled with solution of oxalic acid with free access of air, a golden-yellow liquid is obtained and an insoluble residue of mixed white and blue substances is formed. The latter consists of lead oxalate and Prussian blue, whilst the colour of the liquid is due to ferrous oxalate dissolved in excess of the oxalic acid. A strong odour of hydrogen cyanide is also perceptible. The reaction may be expressed by the following formulæ: (1) $Pb_2Fe(CN)_6 + 2C_2O_4H_2 = 2PbC_2O_4 + H_4Fe(CN)_6$; (2) $7H_4Fe(CN)_6 + O_2 = 2H_2O + 24HCN + Fe_4[Fe(CN)_6]_3$; (3) $H_4Fe(CN)_6 + C_2O_4H_2 = 6HCN + FeC_2O_4$. L. DE K.

Action of Ammonium Chloride on Potassium Ferricyanide. JOH. MATUSCHEK (*Chem. Zeit.*, 1905, **29**, 439—440).—The cyanide, $K(NH_4)_2Fe(CN)_6$, is formed by the action of ammonium sulphate or of ammonium chloride on potassium ferricyanide, whilst the cyanide, $(NH_4)_3Fe(CN)_6$, is produced as an intermediate product, thus,

$$2K_3Fe(CN)_6 + 3(NH_4)_2SO_4 = 3K_2SO_4 + Fe(CN)_6,2(NH_4)_3.$$

By prolonged boiling of a solution containing the cyanide,

$$K(NH_4)_2Fe(CN)_6,$$

in presence of potassium ferricyanide and ammonium chloride, potassium ferrocyanide is produced owing to the dissociation of the ammonium chloride, thus,

$$12[K_3Fe(CN)_6] + 16NH_3 = 9[K_4Fe(CN)_6] + 3[(NH_4)_4Fe(CN)_6] + 4N;$$

the hydrogen chloride, formed by the dissociation of the ammonium chloride, liberates hydroferrocyanic and hydroferricyanic acids from their respective salts present, and then Prussian blue is formed. A. McK.

Methylazoimide. OTTO DIMROTH and WILHELM WISLICENUS (*Ber.*, 1905, **38**, 1573—1576).—Crude sodium azoimide (Dennis and Browne, Abstr., 1904, ii, 558) is dissolved in water, the solution, after being freed from ammonia by a current of air, is gently warmed in a reflux apparatus, and methyl sulphate added drop by drop; the methylazoimide evolved is passed over calcium chloride and soda-lime and condensed in a cooled U-tube. *Methylazoimide*, MeN_3, is a colourless liquid, which boils at 20—21°, has an ethereal but unpleasant odour, explodes when heated above 500°, and has a sp. gr. 0·869 at 8°/15°. G. Y.

Organic Silicon Compounds. FRITZ TAURKE (*Ber.*, 1905, **38**, 1661—1670).—The following compounds are prepared by the interaction of silicon-chloroform and the corresponding alcohol.

Propyl orthosilicoformate, $SiH(OPr)_3$, is a transparent, colourless, strongly-smelling liquid with a sweet taste; it boils at 191—192° and has a sp. gr. 0·885 at 19·5°/4°. *Butyl orthosilicoformate* distils at

240—242°; *amyl orthosilicoformate* boils at 300—305° and has a sp. gr. 0·895 at 15°/4°.

*Silicotetra*iso*amyl*, $Si(C_5H_{11})_4$, prepared by the interaction of silicon tetrachloride, sodium, and *iso*amyl chloride, is a colourless, odourless liquid boiling at 275°. *Silicotri*iso*amyl hydride*, $SiH(C_5H_{11})_3$, is a colourless liquid boiling at 245°, which burns with a luminous flame; *silicotri*iso*amyl oxide*, $Si_2(C_5H_{11})_6O$, is a glycerine-like, colourless oil, which fluoresces faintly and distils at 360—370°. *Silicotri*iso*amyl bromide* is a heavy, yellow, fuming liquid boiling at 278—280°.

*Tri*iso*amylsilicol*, $OH{\cdot}Si(C_5H_{11})_3$, prepared by the action of aqueous ammonia on the bromide, is a clear liquid of characteristic odour, boiling at 269—270°. *Silicotri*iso*butyl hydride* boils at 204—206°; the corresponding *bromide* is a yellow, fuming liquid, heavier than water, which boils at 245°.

Silicon tetrachloroethoxide, $Si(OC_2H_4Cl)_4$, prepared by the interaction of glycol with silicon tetrachloride, whereby ethylenechlorohydrin is formed, and further treatment of this with silicon chloride, boils at 177—180° under 8 mm. pressure. *Silicon tetrachloropropoxide*, $Si(OC_3H_6Cl)_4$, boils at 176° under 4 mm. pressure.

By the interaction of silicon chloride and ethylene glycol, a colourless, amorphous *compound*, $2SiO_2,C_2H_4(OH)_2$, is obtained.

Several statements with regard to silicon compounds in chemical literature are corrected. E. F. A.

Grignard's Reaction with Dihaloids. FELIX B. AHRENS and ADOLF STAPLER (*Ber.*, 1905, **38**, 1296—1298. Compare Grignard and Tissier, Abstr., 1901, i, 316).—The action of ethylene dibromide on magnesium in ethereal solution leads to the formation of the *additive* compound, $C_2H_4Br_2Mg,C_4H_{10}O$, which separates in grey, transparent crystals, and yields ether and ethyl bromide with water, and the crystalline *additive* compound, $MgBr{\cdot}O{\cdot}CHPh{\cdot}CH_2{\cdot}CH_2Br,C_4H_{10}O$, when shaken with benzaldehyde in ethereal solution. In the presence of small quantities of iodine, the action leads to the formation of magnesium bromide and an *oil*, which, with benzaldehyde, forms $MgBr{\cdot}O{\cdot}CHPh{\cdot}CH_2{\cdot}CH_2{\cdot}CHPh{\cdot}O{\cdot}MgBr$, which is obtained as a yellow powder and melts at 160—164°. These magnesium derivatives of ethylene dibromide yield similar compounds with other aromatic aldehydes.

In ethereal solution, in presence of iodine, trimethylethylene dibromide and magnesium form a crystalline substance (magnesium bromide?) and an *oil*, which, with benzaldehyde, yields a white, crystalline *powder*, $MgBr{\cdot}O{\cdot}CHPh{\cdot}CHMe{\cdot}CMe_2Br$, sintering at 185°.

G. Y.

Friedel and Crafts' Reaction. V. Formation of Dichlorodiphenylmethane by the Action of Carbon Tetrachloride on Benzene. JACOB BOESEKEN (*Rec. Trav. chim.*, 1905, **24**, 1—5. Compare Abstr., 1903, i, 617, and 1904, i, 384).—When benzene is added gradually to a mixture of aluminium chloride and carbon tetrachloride, a liquid additive *product* of dichlorodiphenylmethane and

aluminium chloride is formed, which on further treatment with benzene furnishes triphenylmethane chloride, and when washed with water yields dichlorodiphenylmethane. The yield of the latter by this process is from 80 to 90 per cent. of the theoretical.

Toluene under the same conditions yields a mixture of dichloroditolylmethanes in which the para-derivative predominates. With xylene, a certain amount of resinification occurs, but the crude product, when warmed with acetic acid, yields an oil which boils at 202° under 8 mm. pressure, and is probably 1 : 3 : 1′ : 3′-tetramethylbenzophenone and may be identical with the dixylyl ketone prepared by Rilliet and Ador (*J. pr. Chem.*, 1890, **41**, 9). With anisole, only traces of the corresponding dimethoxybenzophenone are produced, probably as the result of the formation of a resistant additive product of anisole and aluminium chloride. T. A. H.

Friedel and Crafts' Reaction. VI. JACOB BOESEKEN (*Rec. Trav. chim.*, 1905, **24**, 6—18. Compare Abstr., 1900, i, 349; 1901, i, 474; 1903, i, 617, 626; 1904, i, 384; this vol., i, 268, and preceding abstract).—It is shown that this reaction can only proceed when the halogen atom of the haloid used can be rendered active by the catalytic agent. The activity and the quantity of the latter required in any particular case are determined by the possibility of the formation of additive compounds from the parent substances or the resulting product and the catalytic agent. Condensations illustrating these points are referred to in the original. T. A. H.

Preparation and Nitration of *m*-Ethyltoluene. EDWARD BARTOW and A. W. SELLARDS (*J. Amer. Chem. Soc.*, 1905, **27**, 369—373).—A method is described for the preparation of *m*-ethyltoluene by a modification of the Fittig synthesis.

Dinitro-m-*ethyltoluene*, prepared by slowly adding *m*-ethyltoluene to fuming nitric acid cooled in a freezing mixture, forms an oil which undergoes decomposition when heated, but can be distilled with steam. On reduction with tin and hydrochloric acid, a small quantity of a diamine is formed which, when treated with nitrous acid, gives a compound analogous to Bismarck brown, thus indicating that the amino-groups are in the meta-position.

s-*Trinitro*-m-*ethyltoluene*, prepared by adding *m*-ethyltoluene to fuming nitric acid and warming the product with a mixture of fuming nitric and concentrated sulphuric acids, forms nearly colourless crystals and melts at 86°. E. G.

***o*-Fluoronitrobenzene and other Aromatic Fluoro-derivatives.** M. HOLLEMAN (*Rec. Trav. chim.*, 1905, **24**, 26—32. Compare Abstr., 1904, i, 232 and 486, and this vol., i, 41).—*o*-Fluoronitrobenzene, prepared by oxidising with copper sulphate the 4-fluoro-3-nitrophenylhydrazine obtained by reducing the product of the diazotisation of 4-fluoro-3-nitroaniline, boils at 115·5° under 22 mm. pressure, solidifies on refrigeration, and then melts at −8°.

4-Fluoro-3-nitrobenzenesulphonic acid may be prepared by sul-

phonating fluorobenzene and nitrating the sulphonic acid obtained; it is not altered by steam and sulphuric acid at 180—200°.

o-*Fluorobenzoic acid* may be prepared by the oxidation of *o*-fluorotoluene; it melts at 119—120°, and does not lose the fluorine atom when heated with ammonia and calcium chloride at 200°.

T. A. H.

Iodoso-, Iodoxy-, and Iodonium Compounds from *s*-Iodoxylene. Conrad Willgerodt and Friedrich Schmierer (*Ber.*, 1905, **38**, 1472—1478).—Full details for the preparation of *s*-xylidine are given. A quantitative yield of aceto-4-*m*-xylidide is obtained when the base is boiled with 3 equivalents of acetic acid for 7 hours. A good yield of 6-nitro-2:4-dimethylacetanilide is obtained when the above acetyl derivative is nitrated with 5 times its weight of fuming nitric acid of sp. gr. 1·48 at a low temperature; when hydrolysed with concentrated sulphuric acid for 10 minutes at 125°, it yields the corresponding nitroxylidine, from which the amino-group may be eliminated in the usual manner; the *s*-nitroxylene thus obtained yields *s*-xylidine on reduction.

s-Iodoxylene yields a *dichloride*, $C_6H_3Me_2{\cdot}ICl_2$, in the form of yellow, compact needles decomposing at 70°. When kept in a stoppered vessel, it loses the whole of its chlorine within 12—14 hours.

The *iodoso*-compound has been obtained in an amorphous form only. The *acetate*, $C_6H_3Me_2{\cdot}I(OAc)_2$, crystallises in colourless prisms melting at 181°, the *basic sulphate*, $[C_6H_3Me_2{\cdot}I(OH)]_2SO_4$, is extremely unstable and melts and decomposes at 120° The *basic nitrate*, $C_6H_3Me_2{\cdot}I(OH){\cdot}NO_3$, forms a yellow powder decomposing at 122°.

s-*Iodoxyxylene*, $C_6H_3Me_2{\cdot}IO_2$, crystallises from hot water in plates and explodes at 216°.

Di-s-*xylyliodonium hydroxide*, $I(C_6H_3Me_2)_2{\cdot}OH$, obtained by decomposing a solution of the iodide with silver oxide and evaporating in a desiccator, crystallises in beautiful white needles, and is the only iodonium hydroxide so far obtained as a solid.

The *iodide*, $I(C_6H_3Me_2)_2{\cdot}I$, decomposes at 164°, the *bromide* crystallises in pale yellow leaflets and melts at 198°. The chloride melts at 186°, and the *dichromate*, $[I(C_6H_3Me_2)_2]_2Cr_2O_7$, forms orange-yellow plates and explodes at 172°.

Iodo-di-s-*xylyliodonium iodide*, $I(C_6H_3Me_2)(C_6H_2IMe_2){\cdot}I$, obtained by Hartmann and Meyer's method (Abstr., 1894, i, 242), forms yellow plates melting at 125°. The *bromide* melts at 149°, the *chloride* at 141°, and the *dichromate* explodes at 95°.

J. J. S.

Intramolecular Oxidation of a Thiol (SH) Group joined to a Benzene Nucleus by a Nitro-group in the ortho-Position. Jan J. Blanksma (*Rec. Trav. chim.*, 1905, **24**, 46—52).—It is shown that in the conversion of trinitro-ψ-cumene into nitro-ψ-cumidinesulphonic acid (Mayer, Abstr., 1887, 659, 953), by the action of ammonium sulphide, ammonium nitrite is formed, and consequently one of the NO_2– groups must be replaced without previous reduction by an –SH group (compare Abstr., 1901, i, 460), which is subsequently

oxidised to $-HSO_3$ by the $-NO_2$ group in the ortho-position relative to it. This observation is confirmed by the fact that sodium hydrogen sulphide or sodium sulphide may be used in place of ammonium sulphide to effect the reduction.

Nitro-ψ-cumidinesulphonic acid, when heated with water in a closed tube at 180°, yields nitro-ψ-cumene; both these substances are converted by bromine in acetic acid into *2-bromo-5-nitro-ψ-cumidine*, which crystallises in bright yellow needles and melts at 150°.

2 : 3 : 5-Trinitro-*p*-xylene behaves similarly when reduced with ammonium, sodium, or sodium hydrogen sulphides. The nitro-*p*-xylidinesulphonic acid so obtained (Fittig, Ahrens, and Mattheides, *Annalen*, 1867, **147**, 24), when heated with water in a closed tube at 180°, yields nitro-*p*-xylidine. When trinitro-*p*-xylene is treated with sodium methoxide and methyl alcohol, it yields 3 : *5-dinitro-2-methoxy*-p-*xylene*, $OMe\cdot C_6HMe_2(NO_2)_2$, which separates from alcohol in almost colourless needles, melts at 60°, and on nitration yields *trinitromethoxy*-p-*xylene* (m. p. 146°); the latter with ammonium sulphide yields *3-nitro-2-methoxy*-p-*xylidine-6-sulphonic acid*, $OMe\cdot C_6Me_2(NO_2)(NH_2)\cdot SO_3H$, which forms colourless crystals, melts at 252°, and, by heating with water at 180° in a closed tube, is converted into *3-nitro-2-methoxy*-p-*xylidine*, melting at 98°. Trinitro-*p*-xylene, when warmed with methylamine (2 mols.) in alcohol in a closed tube, yields 3 : *5-dinitro-2-methylamino*-p-*xylene*, which forms slender orange crystals and melts at 175°; the corresponding *ethylamino*-derivative melts at 133°. Both these substances on nitration yield colourless, crystalline *nitroamines* melting at 94° and 36° respectively.

o-Nitrothiophenol is not reduced by ammonium sulphide, whence it appears that the reaction may be favoured by the presence of methyl groups in the nucleus; it is also accelerated by the action of light.

T. A. H.

Triphenylmethyl. XI. Moses Gomberg and Lee H. Cone (*Ber.*, 1905, **38**, 1333—1344. Compare Abstr., 1901, i, 77, 319, 638, 690; 1902, i, 534, 600, 754; 1903, i, 81, 244; 1904, i, 658, 988).—Triphenylmethyl combines with esters of the fatty acids to form compounds, probably of the type $R\cdot CO\cdot OR'(CPh_3)_2$, in which oxygen is quadrivalent. The compounds with propyl, *iso*butyl, and amyl formates, with methyl, ethyl, and propyl acetates, methyl, ethyl, propyl, and amyl propionates, methyl and ethyl butyrates, and with methyl valerate and ethyl carbonate were analysed. The hydrocarbon does not combine, however, with methyl and ethyl formates. Ethyl oxalate, methyl malonate, ethyl succinate, and ethyl benzoate also combine with triphenylmethyl in the proportion $(CPh_3)_2$: 1 mol. ester. The compounds are crystalline, and are usually analysed by decomposing them at temperatures between 80° and 120° in a current of dry carbon dioxide, the residual triphenylmethyl being weighed. In the analysis of the less volatile esters, the triphenylmethyl is oxidised to the peroxide.

Crystalline compounds of triphenylmethyl with benzene, toluene, ethylbenzene, and the three xylenes were also prepared; in all cases, the product had the composition $(CPh_3)_2$ + 1 mol. hydrocarbon. Tri-

phenylmethyl also combines with a constituent of light petroleum, the product, which is only slowly decomposed in a vacuum, containing about 14 per cent. of the added substance; the nature of the latter is uncertain, but it approximates in composition to C_6H_{10}.

On adding amylene to a solution of triphenylmethyl in carbon disulphide, a crystalline *additive-compound*, $(CPh_3)_2,C_5H_{10}$, separates.

All the additive-compounds described, when subjected to the action of oxygen, give triphenylmethyl peroxide and the corresponding ester or hydrocarbon; they are probably therefore formed by a mere association of their constituents. W. A. D.

Action of Sulphur on Aniline and Aniline Hydrochloride. KARL A. HOFMANN (*Ber.*, 1905, **38**, 1432—1433).—Hinsberg's dithioaniline (this vol., i, 339) has been previously obtained by the author (Abstr., 1895, i, 87). J. J. S.

Mode of Formation of Monosubstituted Urethane Derivatives. F. BODROUX (*Compt. rend.*, 1905, **140**, 1108—1109).—When ethyl carbonate is gradually added to an ethereal solution or suspension of the magnesium halogen compound of a primary aromatic amine, an energetic reaction takes place and a derivative of urethane is obtained. From aniline, ethyl phenylcarbamate is formed according to the equation: $2NHPh\cdot MgI + CO(OEt)_2 + H_2O = NHPh\cdot CO_2Et + NH_2Ph + OEt\cdot MgI + MgI\cdot OH$. The yield of ethyl phenylcarbamate is increased from 50 to 80 per cent. if the ether is boiled for several hours after the addition of the ethyl carbonate, or if the latter is added very slowly to the boiling ethereal solution. A small quantity of *s*-diphenylcarbamide is produced in the change according to the equation: $3NHPh\cdot MgI + CO(OEt)_2 + H_2O = CO(NHPh)_2 + NH_2Ph + 2OEt\cdot Mg\cdot I + OH\cdot MgI$.

o- and *p*-Toluidines and β-naphthylamine yield the corresponding urethanes by the same reaction. Ethyl carbonate has no action on the magnesium halogen derivative of ammonia. H. M. D.

Reduction of Oximes and Hydrazones with Zinc Dust and Glacial Acetic Acid. HARTWIG FRANZEN (*Ber.*, 1905, **38**, 1415—1417).—Benzaldoxime yields a mixture of benzylamine and dibenzylamine when reduced with zinc dust and glacial acetic acid in alcoholic solution. Similarly, from *o*-chlorobenzaldoxime a mixture of *o*-chlorobenzylamine and di-*o*-chlorobenzylamine is obtained. o-*Chlorobenzylamine* is a yellow oil, boiling at 103—104° under 11 mm. pressure; the *hydrochloride* forms colourless plates melting at 215—216°; the *picrate* forms broad, yellow needles and melts and decomposes at 217°. E. F. A.

Preparation of Certain Amines. LATHAM CLARKE (*Amer. Chem. J.*, 1905, **33**, 496—500).—The following method is recommended for the preparation of dimethyl-*p*-toluidine. *p*-Toluidine is boiled with methyl iodide in a reflux apparatus for 30—40 minutes. The excess of methyl iodide is removed by distillation, the last portion being expelled by passing a current of air through the warm liquid.

The product is treated with a strong solution of potassium hydroxide, and the oily layer is separated and dried with solid potassium hydroxide. The oil is again treated with methyl iodide under the same conditions as before; the excess of methyl iodide is removed, potassium hydroxide solution is added to the residue, and the oil which separates is withdrawn and dried as before. On distilling the product, pure dimethyl-*p*-toluidine is obtained. Dimethyl-*o*-toluidine may be prepared in the same manner.

*Methyl*iso*amylamine*, prepared by the above method, is a colourless liquid which boils at 95°.

*Dimethyl*iso*amylamine* boils at 98° and has a strong odour.

The method has also been found to be of value for the preparation of benzyldimethylamine, but is not suitable for the preparation of α- and β-naphthyldimethylamines. E. G.

Evidence for the Possibility of Resolving an Optically Active Compound without actually Resolving it and without the Aid of Optically Active Substances. Ernst Mohr (*J. pr. Chem.*, 1905, [ii], **71**, 305—357. Compare Abstr., 1904, i, 653; 1904, ii, 689; Kipping and Hall, Trans., 1901, **79**, 442; Kipping and Salway, Trans., 1904, **85**, 438).—This is chiefly a detailed account of work previously published.

When boiled with 6*N*-hydrochloric acid for 15 hours in a reflux apparatus, α-phenylethylamine is hydrolysed with formation of ammonia. Under the same conditions, ammonia is obtained also from benzhydrylamine (Darapsky, Abstr., 1903, i, 367).

Dihydrocinnamoylpiperidide, formed by the action of dihydrocinnamoyl chloride on piperidine in anhydrous ethereal solution, is obtained as a slightly yellow oil which partly solidifies. The *benzoin* ester of dihydrocinnamic acid, formed by fusing the acid chloride with benzoin or by boiling these substances with sodium carbonate in benzene solution, melts at 61—64°. The *benzylamide*, $CH_2Ph\cdot CH_2\cdot CO\cdot NH\cdot CH_2Ph$, formed by boiling the acid chloride with benzylamine and sodium carbonate in a neutral solvent, crystallises from hot alcohol or light petroleum in slender, white needles or narrow leaflets, or on slow evaporation in rosettes of plates. The *α-phenylethylamide*, formed in the same manner as the benzylamide, crystallises in white needles, is easily soluble in organic solvents, and is hydrolysed when boiled for 20 hours with 6*N*-hydrochloric acid, but not with alcoholic potassium hydroxide.

Ethyl benzylmalonate has n_D 1·487—1·490 at 13—19°; ethyl benzylethylmalonate boils at 173° under 12·5 mm. or at 184° under 18 mm. pressure, has n_D 1·488—1·490 at 13—19°, and on hydrolysis with alcoholic potassium hydroxide yields benzylethylmalonic acid, which forms a white, crystalline mass, melts at 104—114°, and commences to lose carbon dioxide at 128°. Benzylethylacetic acid is formed by heating the malonic acid at 145°, and finally at 180—190°; the chloride is best formed by the action of thionyl chloride on the acid.

The mixture of two racemic modifications of α-phenylethylamides of benzylethylacetic acid, obtained by the action of benzylethylacetyl chloride on α-phenylethylamine in presence of sodium carbonate in ethereal solution, yields on recrystallisation from light petroleum 15·6

per cent. of the less fusible and 55·8 of the more fusible isomeride. The modification melting at 112° crystallises in long, thin, white, glistening needles, is slightly soluble in cold light petroleum, but easily so in other organic solvents, has $[\alpha]_D$ less than $+0·105°$, and, when boiled for 37 hours or heated in a sealed tube at 110—132° for 21 hours, with hydrochloric acid of sp. gr. 1·093, is hydrolysed to the extent of 41 or 63 per cent. respectively, yielding benzylethylacetic acid, but only little α-phenylethylamine. The racemic modification melting at 87—88° crystallises in sheaves of slender, white, silky needles, is more easily soluble in light petroleum than is its isomeride, and is hydrolysed to the extent of 21 per cent. when boiled for 28 hours with hydrochloric acid of sp. gr. 1·093, or to 82 per cent. when heated with hydrochloric acid of sp. gr. 1·110 at 110—150° for 20·5 hours in a sealed tube. G. Y.

Condensation of Benzylideneaniline with Ethylacetonedicarboxylate. CHARLES MAYER (*Bull. Soc. chim.*, 1905, [iii], 33, 498—500. Compare Abstr., 1904, i, 832).—Schiff (Abstr., 1898, i, 237) has found that when ethyl acetonedicarboxylate is treated with benzylideneaniline the additive product,

$$CO[CH(CO_2Et)\cdot CHPh\cdot NHPh]_2,$$

is formed. The author has repeated this work, and finds that, when the reaction takes place in benzene solution, Schiff's additive product (m. p. 134°) is obtained, but that when alcohol is employed as a solvent the substance formed is probably *ethyl triphenylpiperidonedicarboxylate*, $NPh<\begin{matrix}CHPh\cdot CH(CO_2Et)\\CHPh\cdot CH(CO_2Et)\end{matrix}>CO$, although it may have the constitution $NHPh\cdot CHPh\cdot CH(CO_2Et)\cdot CO\cdot C(CO_2Et):CHPh$. This crystallises in large, colourless lamellæ, melts at 124°, and is very soluble in benzene or ether, less so in alcohol. This substance may also be obtained by boiling Schiff's additive product with alcohol. The author considers that Schiff's opinion that the additive product exists in three forms is not justified, and he points out that the same question has arisen with regard to the similar product formed with benzylideneaniline and ethyl acetoacetate (Rabe, Abstr., 1903, i, 62). T. A. H.

Condensation of Phenol with Formaldehyde. FRITZ HENSCHKE (D.R.-P. 157553 and 157554).—When an alkaline solution of phenol is heated with formaldehyde at 100° in an autoclave, a solution is obtained which has strong antiseptic properties and is free from the odour of phenol. Acids precipitate a bulky, pale-yellow powder, insoluble in water or chloroform, soluble in alcohol, acetone, dilute sodium hydroxide, or ammonia. It decomposes on heating or on boiling its alkaline solution.

When iodine is added to the above alkaline solution, followed by an acid, a *compound* is obtained in which the iodine is combined organically. C. H. D.

Picric Acid and 4:6-Dinitro-2-aminophenol (Picramic Acid). JULES ALOY and A. FRÉBAULT (*Bull. Soc. chim.*, 1905, [iii], 33, 495—498. Compare Abstr., 1904, i, 870).—Methods for the prepara-

tion of picramic acid from picric acid by the use of (1) zinc and ammonia solution and (2) sodium hyposulphite as reducing agents are described.

2-Chloro-4 : 6-dinitrophenol, prepared by Prud'homme and Rabaut's method (Abstr., 1892, 705), melts at 109°; it usually contains a small quantity of a crystalline substance which sublimes at 115—120°.

The first product of the diazotisation of picramic acid decomposes giving rise to a yellow, crystalline substance, which melts at 168—169° and is highly inflammable and explosive.

Picric acid may be detected in solutions containing only one part of the acid in 100,000 by the coloration produced on addition of sodium hyposulphite in presence of ammonia. T. A. H.

Dinitro-derivatives of *p*-Aminophenol. FRÉDÉRIC REVERDIN and AUGUSTE DRESEL (*Ber.*, 1905, **38**, 1593—1599. Compare this vol., i, 51).—*Dinitro-*p*-acetylaminophenyl acetate*, formed by nitration of *p*-acetylaminophenyl acetate with nitric acid of sp. gr. 1·52 at − 10°, crystallises in slender, white needles, melts at 223—224°, and is hydrolysed by acids to 3 : 5-dinitro-4-aminophenol, melting at 230—231°, by sodium carbonate in aqueous solution to 3 : 5-dinitro-4-acetylaminophenol melting at 182°.

3 : 2′ : 4′-*Trinitro-4-hydroxydiphenylamine*, formed by heating 2-nitro-4-aminophenol with 1-chloro-2 : 4-dinitrobenzene in alcoholic solution, crystallises in orange leaflets, melts at 232—233°, and forms a yellow, crystalline *sodium* salt and an *acetyl* derivative which crystallises in lemon-yellow prisms and melts at 167—168°.

2 : 4-*Dinitrophenyl 3-nitro-4-aminophenyl ether* is formed by the action of 1-chloro-2 : 4-dinitrobenzene on 3-nitro-4-aminophenol in alcoholic solution; it crystallises in yellow leaflets and melts at 188°.

3 : 5-Dinitro-4-aminophenol crystallises in glistening leaflets or long, red needles, depending on the concentration of the solution, sublimes at 150°, and dissolves in aqueous alkali hydroxides or carbonates to a violet solution which becomes red and finally brown. With 1-chloro-2 : 4-dinitrobenzene it yields the *ether*, $C_6H_3(NO_2)_2{\cdot}O{\cdot}C_6H_2(NO_2)_2{\cdot}NH_2$, which crystallises in lemon-yellow needles, melts at 225—226°, and forms an *acetyl* derivative, $C_{14}H_9O_{10}N_5$, crystallising in needles and melting and decomposing at 238°. When stirred for some hours with sodium nitrite in cooled concentrated sulphuric acid solution, 3 : 5-dinitro-4-aminophenol forms the yellow, crystalline *diazonium* salt, which explodes when heated, and, when dried and boiled with absolute alcohol, yields 3 : 5-dinitrophenol (m. p. 122°).

2 : 5-Dinitro-4-acetylaminophenoxyacetic acid (Howard, Abstr., 1898, i, 29) is hydrolysed by sulphuric acid to 2 : 5-*dinitro-4-aminophenoxyacetic acid*, which crystallises in hexagonal, prismatic needles, or small, red prisms, commences to decompose at 190°, melts at 204—205°, does not react with chlorodinitrobenzene, and is converted into the acetyl derivative (m. p. 204—205°) when warmed with acetic anhydride and sulphuric acid; the *sodium* salt crystallises in red, glistening leaflets.

When diazotised in the same manner as 3 : 5-dinitro-4-aminophenol, *iso*picramic acid (Dabney, Abstr., 1884, 308; Meldola, Trans., 1902, 81, 988) forms explosive *diazonium* salts, which, when boiled with

absolute alcohol, yield 2 : 6-dinitrophenol (m. p. 64°) and are converted by cuprous chloride and potassium iodide into 4-chloro-2 : 6-dinitrophenol and 4-iodo-2 : 6-dinitrophenol respectively. *iso*Picramic acid and dinitrochlorobenzene, when boiled in alcoholic sodium acetate solution, form 3 : 5 : 2′ : 4′-*tetranitro-4-hydroxydiphenylamine*,

$$C_6H_3(NO_2)_2 \cdot NH \cdot C_6H_2(NO_2)_2 \cdot OH,$$

which is a yellow, insoluble powder melting at 236°; the *sodium* salt crystallises in brown needles; the *acetyl* derivative crystallises in yellow needles and melts at 210°. G. Y.

Nitration and Reduction of *s*-Dinitrophenetole. JAN J. BLANKSMA (*Rec. Trav. chim.*, 1905, **24**, 40—45. Compare Abstr., 1903, i, 623).—When dinitrophenetole is warmed with nitric acid of sp. gr. 1·44 and sulphuric acid at 100° for 1 hour, 2 : 3 : 5-*trinitrophenetole* is formed; this separates from alcohol in bright yellow crystals and melts at 80°. Ammonia converts it into 3 : 5-*dinitro-2-phenetidine*, $OEt \cdot C_6H_2 \cdot NH_2(NO_2)_2$, which forms yellow crystals and melts at 195°. With methylamine, 3 : 5-*dinitro-2-methylaminophenetole* is produced; this forms orange crystals, melts at 174°, and on nitration furnishes the corresponding *nitroamine*, which is colourless and melts at 69°. 3 : 5-*Dinitro-2-ethylaminophenetole*, similarly obtained, forms orange crystals and melts at 137°; the corresponding *nitroamine* melts at 72°. 3 : 5-*Dinitro-2-anilinophenetole*, $OEt \cdot C_6H_2(NO_2)_2 \cdot NHPh$, crystallises in yellow needles and melts at 155°.

2 : 3 : 5-Trinitrophenetole is converted by sodium ethoxide and ethyl alcohol into *dinitrocatechol diethyl ether*, which forms nearly colourless crystals and melts at 78°. On nitration, this yields 3 : 4 : 5-*trinitrocatechol diethyl ether*, which is colourless and melts at 122°. This substance may also be prepared by the direct nitration of catechol diethyl ether.

If 2 : 3 : 5-trinitrophenetole is warmed for 2 hours with nitric acid of sp. gr. 1·52 and sulphuric acid at 100°, 2 : 3 : 5 : 6-*tetranitrophenetole* is formed, which separates from alcohol in bright yellow crystals, melts at 115°, and is converted by sodium ethoxide and ethyl alcohol into *dinitrophloroglucinol triethyl ether*, $C_6H(OEt)_3(NO_2)_2 = 1:3:5:2:6$ (compare *loc. cit.*).

On reduction with hydrogen sulphide in presence of ammonia, *s*-dinitrophenetole yields 3-*nitro-5-ethoxyaniline*, which crystallises from water in long, yellow needles, melts at 115°, and with bromine in acetic acid gives 2 : 4 : 6-*tribromo-3-nitro-5-ethoxyaniline*, which forms yellow crystals and melts at 102°.

s-Dinitroanisole, on reduction in the same way, yields 3-*nitro-5-methoxyaniline*, which forms orange crystals, melts at 118°, and furnishes a bright yellow *acetyl*-derivative melting at 193°; the *tribromo*-derivative, prepared like the higher homologue, melts at 110° and yields 3 : 5-diaminoanisole on reduction with tin and hydrochloric acid. T. A. H.

Attempts to Synthesise Fluorene Derivatives. OTTO DIELS and FELIX BUNZL (*Ber.*, 1905, **38**, 1486—1498. Compare *Ber.*, 1873, **6**, 187; Staedel, Abstr., 1895, i, 147; Graebe and Ullmann, *ibid.*, 147).—Attempts have been made to prepare di-*o*-halogen derivatives

of diphenylmethane, and to transform these into fluorene derivatives by the removal of the halogen.

Ethyl sodiomalonate and ethyl sodioacetoacetate react with 1 : 2-dibromo-4-nitrobenzene (Hosaeus, Abstr., 1894, i, 17), yielding Staedel's 2-bromo-4-nitrophenetole (Abstr., 1883, 585). On hydrolysis with sulphuric acid, it yields 2-bromo-4-nitrophenol, which melts at 113—114°, and not at 102° as stated by Brunck (*Zeit. Chem.*, 1867, 204).

Formaldehyde condenses with *p*-bromophenetole in the presence of sulphuric acid at low temperatures, yielding 5 : 5'-*dibromo*-2 : 2'-*diethoxydiphenylmethane*, $CH_2(C_6H_3Br\cdot OEt)_2$. It crystallises from acetic acid in well-developed prisms, melts at 143°, and dissolves readily in warm acetone or ethyl acetate, and in cold carbon disulphide or benzene. On oxidation with an acetic acid solution of chromic acid, it yields 5 : 5'-*dibromo*-2 : 2'-*diethoxybenzophenone*, which crystallises from alcohol in flat plates, melting at 99—100° and readily soluble in benzene or chloroform. The *phenylhydrazone*, $C_{23}H_{22}O_2N_2Br_2$, sinters at 130° and melts at 133°.

When hydrolysed with concentrated hydrochloric acid at 160—170°, or with aluminium chloride at 130—140°, it yields a *compound*, $C_{15}H_{12}O_3Br_2$, which has the composition of a monoethyl ether of dibromodihydroxybenzophenone, but its properties do not agree with such a constitution. It crystallises from acetic acid, melts at 114°, and yields a mono-*potassium* derivative, which is only stable in the presence of a large excess of alkali.

When boiled with aqueous alcoholic potash, it yields 2 : 7-dibromoxanthone (Perkin, Trans., 1883, **43**, 193).

Details of the preparation of *m*-bromophenol are given (compare Wurster and Noelting, *Ber.*, 1874, **7**, 905). When etherified by means of methyl sulphate and alkali, it yields m-*bromoanisole* as a colourless oil distilling at 210—211° under 752 mm. pressure. *m*-Bromoanisole and benzoyl chloride react with aluminium chloride in the presence of carbon disulphide yielding a mixture from which two substances have been isolated: a *compound*, $C_{14}H_{10}O_2Br_2$, which crystallises from alcohol, melts at 121° and dissolves sparingly in the usual organic solvents, and a *compound*, $C_{15}H_{12}O_2Br_2$, of phenolic nature, which distils at 305—310°. J. J. S.

Action of Phosphorus on Organic Compounds. II. HERMANN WICHELHAUS (*Ber.*, 1905, **38**, 1725—1728. Compare Abstr., 1903, i, 818).—Water and dinaphthyl oxide are formed by the action of hydrogen phosphide on *α*-naphthol at 200°, whilst naphthalene is formed at 300°. When *α*-naphthol is heated with yellow phosphorus at 300°, a mixture of naphthalene and dinaphthyl oxide is produced. Phosphorus chloride is formed when chloranil is heated with red phosphorus, and also a substance containing 44 per cent. of chlorine and yielding an acetyl derivative and an anilide. A. McK.

5-Aminoeugenol. GIUSEPPE ODDO and ERNESTO PUXEDDU (*Gazzetta*, 1905, **35**, i, 74—77).—5-*Aminoeugenol*,

$C_3H_5\cdot C_6H_2(OMe)(OH)\cdot NH_2$ [$C_3H_5 : OMe : OH : NH_2 = 1 : 3 : 4 : 5$],

best prepared by reducing benzeneazoeugenol with tin and hydrochloric acid, crystallises from light petroleum or water in shining, white scales, melting at 114°, and is soluble in acids or dilute alkali solutions, and readily so in the more common organic solvents. It undergoes a slight change in the air, assuming a grey colour, and is readily decomposed by concentrated hydrochloric acid. It decolorises bromine water or potassium permanganate solution and reduces Fehling's solution. The addition of a few drops of ferric chloride solution to its dilute hydrochloric acid solution yields a dark brown coloration which exhibits fluorescence in dilute solution. Its *hydrochloride* is white and melts at above 200°, and its *platinichloride* is obtained as a dark greenish-yellow, crystalline powder which does not melt or decompose at 230°. Its *acetyl* derivative, $C_{12}H_{15}O_3N$, crystallises from water in silky, white needles, melts at 132° and is very soluble in all organic solvents; it decolorises bromine water and permanganate solution, but yields no coloration with ferric chloride. Another acetyl derivative, melting at 86°, has also been obtained, but has not yet been examined. T. H. P.

[2-Hydroxydibenzyl.] STANISLAUS VON KOSTANECKI (*Ber.*, 1905, 38, 1548).—2-Hydroxydibenzyl had been described by Stoermer (Abstr., 1904, i, 181, 182) prior to the publication of Rost, Szabrański, and Kostanecki's paper (this vol., i, 341). A. McK.

Reactions of Certain Ethylenic Compounds with Mercuric Acetate in Glacial Acetic Acid Solution. Mercury Resorcinolmercuriacetate and Phloroglucinoltrimercuriacetate. ALEXANDRE LEYS (*J. Pharm. Chim.*, 1905, [vi], 388—396).—Benzenoid hydrocarbons, benzaldehyde, phenyl salicylate, phenolphthalein, and benzoic, cinnamic, phthalic, *o*-, *m*-, and *p*-hydroxybenzoic and picric acids give no precipitates with a warm solution of mercuric acetate in glacial acetic acid, but the hydroxybenzoic acids and phenolphthalein give faint rose colorations.

With monohydric phenols, dissolved in warm glacial acetic acid, a yellow colour is produced, and a white solid gradually separates. Catechol, quinol, and anthraquinone give brown colorations, mercuric acetate being deposited, whilst resorcinol at 60—70° gives a deep yellow precipitate.

Pyrogallol, phloroglucinol, and gallic acid give yellow, and tannin red, precipitates.

Aniline and toluidine give no reaction, but diazobenzenesulphonic acid and phenylhydrazine cause evolution of gas and the formation of yellow and red precipitates respectively.

The yellow *mercury resorcinolmercuriacetate*, $HgO_2{:}C_6H_3{\cdot}Hg{\cdot}OAc$, decomposes on heating without fusing. It is insoluble in water, organic media, most salt solutions, alkalis, and dilute sulphuric and phosphoric acids, soluble in dilute hydrochloric and nitric acids, potassium cyanide, thiocyanate, bromide and iodide, sodium sulphite, thiosulphate and hydrogen sulphite, mercuric sulphide separating from the two latter solutions, a reaction at once given by sodium sulphide.

With the solution in potassium iodide, iodine produces a violet precipitate unaltered by thiosulphate.

Phloroglucinoltrimercuriacetate, $C_6H_3(O\cdot Hg\cdot OAc)_3$, resembles the resorcinol compound in solubility, but is insoluble in dilute nitric acid, and iodine produces, in the potassium iodide solution, a brown colour discharged by thiosulphate. G. D. L.

Influence of Alkaline Substances on Spontaneous Oxidation. EDUARD SCHAER (*Arch. Pharm.*, 1905, **243**, 198—217. Compare Feder, this vol., i, 150).—As is well known, tannic acid, pyrogallol, quinone, aloin, chrysarobin, and brazilin are substances which undergo auto-oxidation, their solutions darkening in the air. This process is much accelerated by the presence of even small quantities of alkalis, of salts the solution of which in water has an alkaline reaction, and of alkaloids; a few mg. of these were added to each 10 c.c. of a dilute solution of the substance that undergo oxidation.

Special stress is laid on a suggestion that the darkening in colour observed when many pharmaceutical extracts are concentrated may be a consequence of the presence of ammonium nitrite, which Schönbein has shown to appear in water that is being evaporated. Besides effecting any specific oxidations characteristic of nitrites, it is one of those substances which accelerate auto-oxidation (its aqueous solution has an alkaline reaction). C. F. B.

Conversion of Hydroaromatic Alcohols into Benzene Derivatives. KARL AUWERS [and, in part, M. HESSENLAND] (*Ber.*, 1905, **38**, 1697—1711. Compare Abstr., 1904, i, 26).—In the preparation of tertiary alcohols from cyclic ketones by the Grignard synthesis, it is advisable to use double the theoretical amount of magnesium alkyl iodide to carry out the reaction in concentrated solution and to immediately decompose with water.

1-*Hydroxy*-4-*methyl*-4-*dichloromethyl*-1-*ethyldihydrobenzene*, $C_{10}H_{14}OCl_2$, has been obtained in the form of colourless, compact prisms melting at 45—50°. When heated at 80° for 1—1·5 hours and then distilled under reduced pressure, it yields 1-*methyl*-4-*dichloro*iso*propylbenzene*, $C_6H_4Me\cdot CHMe\cdot CHCl_2$, as a liquid distilling at 143—145° under 30 mm. pressure or at 247—249° under atmospheric pressure. It has a sp. gr. 1·1563 at 20°/20° and n_D 1·53356 at 20°. When reduced with sodium and boiling alcohol, it yields cymene, which was identified by conversion into pentabromotoluene melting at 280°, and hydroxycumic and *p*-*iso*propenylbenzoic acids.

When the methyldichloro*iso*propylbenzene is oxidised with chromic anhydride, it yields *dichloro*-p-*cumic acid*, $CO_2H\cdot C_6H_4\cdot CHMe\cdot CHCl_2$, in the form of flat needles melting at 113—114°, and when heated with water at 170—180° it is converted into an *aldehyde*, the *semicarbazone* of which melts at 157—159° and has the composition $C_{11}H_{15}ON_3$. The constitution of the aldehyde has not yet been determined.

An alcoholic solution of potassium hydroxide transforms the chloride into *β*-*chloro*-*a*-p-*dimethylstyrene*, $C_6H_4Me\cdot CMe\colon CHCl$, which distils at 111—114° under 15 mm. pressure. When oxidised with permanganate, the styrene derivative is converted into *p*-methylacetophenone, the *semicarbazone* of which melts at 205°. J. J. S.

Nitrobenzyl Ethers. GIOVANNI ROMEO (*Gazzetta*, 1905, **35**, i, 111—120).—p-*Nitrobenzyl methyl ether*, $NO_2\cdot C_6H_4\cdot CH_2\cdot OMe$, prepared by the action of sodium methoxide on *p*-nitrobenzyl chloride in methyl-alcoholic solution, separates from light petroleum in large prisms melting at 29—30° and slowly turning green in the air, sublimes as a white powder, and is readily soluble in alcohol, benzene, or acetic acid.

p-*Aminobenzyl methyl ether*, $NH_2\cdot C_6H_4\cdot CH_2\cdot OMe$, obtained by reducing a solution of the corresponding nitro-compound in sodium hydroxide by means of ferrous sulphate, is a dense, almost colourless oil distilling at 164—167° under 40 mm. pressure and dissolves in water, alcohol, or ether; with oxalic acid in alcoholic solution it yields a white, crystalline *oxalate* melting at 116°.

p-*Benzoylaminobenzyl methyl ether*, $NHBz\cdot C_6H_4\cdot CH_2\cdot OMe$, prepared by the action of benzoyl chloride on the previous compound in potassium hydroxide solution, crystallises from aqueous alcohol or a mixture of benzene and light petroleum in shining, silvery scales melting at 111—113°, and is readily soluble in alcohol or benzene and slightly so in light petroleum or water.

In preparing ethyl methyl malonate according to the method given by Züblin (Abstr., 1879, 783), a small proportion of ethyl ethanetetracarboxylate is also obtained.

Ethyl p-*nitrobenzylmethylmalonate*, prepared by the action of *p*-nitrobenzyl chloride on sodium ethyl methylmalonate, crystallises from alcohol or light petroleum in shining needles or monoclinic prisms melting at 59—60·5°, and is soluble in alcohol or benzene and to a moderate extent in light petroleum.

p-*Nitrobenzylmethylmalonic acid*, $NO_2\cdot C_6H_4\cdot CH_2\cdot CMe(CO_2H)_2$, crystallises from xylene in scales or leaflets melting and decomposing at 162—163°, and is soluble in alcohol or water. It forms the following salts: *lead*, white precipitate; *silver*, white, gelatinous precipitate; *ferric*, whitish precipitate; *barium*, white, crystalline precipitate; *calcium*, white, acicular precipitate; *cupric*, pale blue precipitate, which crystallises from water in pale blue, silky needles containing $1\frac{1}{2}H_2O$. The xylene mother liquors from the above acid contain a small proportion of nitrophenyl*iso*butyric acid (see Edeleanu, Trans., 1888, **53** 558), melting at 123°; this acid is also formed on heating *p*-nitrobenzylmethylmalonic acid. T. H. P.

***o*- and *p*-Methoxyphenylethylcarbinols and the Corresponding Anetholes.** CARL HELL and ALEXANDER HOFMANN (*Ber.*, 1905, **38**, 1676—1680).—o-*Methoxyphenylethylcarbinol*, prepared by the action of magnesium ethyl bromide on *o*-methoxybenzaldehyde, is a bright yellow, odourless oil boiling at 138° under 22 mm. and at 251° under 760 mm. pressure; the *phenylcarbamate* forms colourless crystals melting at 102°.

o-Anethole, prepared by distilling the carbinol with a little sulphuric acid, is a colourless oil with a characteristic odour, boiling at 222°; it yields a yellow, crystalline *ψ-nitrosite*, $C_{20}H_{24}O_2,N_4O_6$, melting and decomposing at 123°, also a crystalline *nitrosochloride*, $C_{10}H_{12}O,NOCl$. When care is taken to exclude all traces of acid

impurity during the preparation, *p*-methoxyphenylethylcarbinol is obtained as a colourless, viscous oil, boiling at 143° under 20 mm. and at 261° under the ordinary pressure (compare Klages, this vol., i, 344). E. F. A.

[*p*-Methoxyphenylethylcarbinol.] CARL HELL (*Ber.*, 1905, **38**, 1680—1683).—Polemical (see preceding abstract, also Klages, Abstr., 1904, i, 487, and this vol., i, 344). E. F. A.

Action of Magnesium Phenyl Bromide on Glycine Ethyl Ester. CARL PAAL and ERICH WEIDENKAFF (*Ber.*, 1905, **38**, 1686—1689. Compare Basset, this vol., i, 898).—Glycine ethyl ester (Fischer, Abstr., 1901, i, 192) readily reacts with an excess of an ethereal solution of magnesium phenyl bromide, and the product, after treatment with hydrochloric acid, yields diphenyl and *β-hydroxy-ββ-diphenylethylamine*, $OH\cdot CPh_2\cdot CH_2\cdot NH_2$. The amine crystallises from hot water in colourless, glistening needles, melts at 110—111°, and is readily soluble in most organic solvents. The *hydrochloride* forms colourless needles melting at 192—193° and is readily soluble in water or alcohol. The *nitrate* melts at 203—204° and is only sparingly soluble in cold water or alcohol. The *picrate* melts at 183°; the *aurichloride*, $C_{14}H_{15}ON,HAuCl_4$, crystallises with $1H_2O$, which it loses at 70—80°, and then melts at 119—120°; the *platinichloride* crystallises with $2H_2O$, melts at 155°, or in the anhydrous state at 161°. J. J. S.

Amino-alcohols of the Formula $C_6H_3(OH)_2\cdot CH(OH)\cdot CH_2\cdot NX_2$. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 157300. Compare Abstr., 1904, i, 873; this vol., i, 127).—Aminoacetylcatechol and its derivatives may be reduced to amino-alcohols of the formula $C_6H_3(OH)_2\cdot CH(OH)\cdot CH_2\cdot NX_2$, which resemble the acetyl compounds in physiological properties, but are more active. Various methods of reduction may be employed. Thus aluminium powder and mercuric sulphate reduce methylaminoacetylcatechol sulphate; the *sulphate* of the resulting amino-alcohol is amorphous and gives a green coloration with ferric chloride. Ethylaminoacetylcatechol may be electrolytically reduced in 5 per cent. sulphuric acid solution, using lead electrodes with a diaphragm, and a current density of 0·25 amperes per sq. dm. at 2·5 volts. Sodium amalgam reduces aminoacetylcatechol, the amino-alcohol forming a hygroscopic *hydrochloride*. C. H. D.

Electrolytic Reduction of Aromatic Carboxylic Acids to the Corresponding Alcohols. CARL METTLER (*Ber.*, 1905, **38**, 1745—1753).—When the solution of benzoic acid in a mixture of sulphuric acid and alcohol is electrolysed at 20—30° with lead electrodes and a current strength of 10 amperes, an 85 per cent. yield of benzyl alcohol is obtained. Similarly, *m*-bromobenzoic acid is converted into *m*-bromobenzyl alcohol, *m*-chlorobenzoic acid into *m*-chlorobenzyl alcohol, *o*-chlorobenzoic acid into *o*-chlorobenzyl alcohol, and *p*-chlorobenzoic acid into *p* chlorobenzyl alcohol.

Anthranilic acid is converted into *o*-aminobenzyl alcohol, *m*-nitro-

benzoic acid into *m*-aminobenzyl alcohol, and *m*-hydroxybenzoic acid into *m*-hydroxybenzyl alcohol. Phenyl benzoate is readily converted into phenylbenzyl ether and benzyl benzoate into dibenzyl ether.

A. McK.

Salts of Benzamide with Dicarboxylic Acids. FRANZ HENLE (*Ber.*, 1905, **38**, 1373—1375).—The following salts are easily obtained by dissolving benzamide and the acid in hot water or, better, in alcohol. *Benzamide oxalate*, $2COPh\cdot NH_2,C_2H_2O_4$, crystallises from water in white leaflets and melts at 156—157°. *Benzamide tartrate*, $2COPh\cdot NH_2,C_4H_6O_6$, crystallises from alcohol in leaflets and melts at 137—140°. *Benzamide succinate*, $C_{11}H_{13}O_5N$, crystallises in colourless prisms and melts at 126—128°. An oxalate of diphenylamine could not be obtained.

W. A. D.

Reduction of Benzonitrile and *p*-Tolunitrile. A. FREBAULT (*Compt. rend.*, 1905, **140**, 1036—1038).—By the direct hydrogenation of aromatic nitriles in presence of reduced nickel at 200°, Sabatier and Senderens (this vol., i, 267) obtained only the corresponding hydrocarbons and ammonia. Under modified experimental conditions the author finds that the reaction is similar to that which takes place with the aliphatic nitriles and that primary and secondary aromatic amines can be thus obtained. To ensure uniformity of temperature, the tube containing the reduced nickel is imbedded in iron filings, and a rapid current of hydrogen is passed through it at about 250°, the nitrile being allowed to fall directly into the tube drop by drop.

From benzonitrile, benzylamine and dibenzylamine are obtained in approximately equal quantities, together with a small quantity of crystals, possibly tribenzylamine. From *p*-tolunitrile, *p*-methylbenzylamine and di-*p*-methylbenzylamine are obtained.

H. M. D.

Condensation Product from Anthranilic Acid and Formaldehyde. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 158090).—Anthranilic acid is precipitated from its aqueous solutions, even when very dilute, in the form of a condensation product insoluble in alkali hydroxides. This compound forms large, yellowish-white crystals, which decompose slowly at 150°, and dissolve sparingly in alcohol or hot benzene. The crystals are strongly luminous when rubbed in the dark. Hydrocyanic acid converts it into ω-cyanomethylanthranilic acid.

C. H. D.

Derivatives of Anthranilic Acid. BRONISLAW VON PAWLEWSKI (*Ber.*, 1905, **38**, 1683—1685. Compare Abstr., 1904, i, 316).—N-*Phenylsulphoneanthranilic acid*, $SO_2Ph\cdot NH\cdot C_6H_4\cdot CO_2H$, obtained by heating a xylene solution of anthranilic acid and benzenesulphonic chloride, crystallises from acetic acid in thick, colourless needles, melts at 214—215°, has sp. gr. 1·4255 at 20°/4°, and is only sparingly soluble in the usual organic solvents.

N-*Chloroacetylanthranilic acid*, $CH_2Cl\cdot CO\cdot NH\cdot C_6H_4\cdot CO_2H$, crystallises from alcohol in long, slender needles melting at 186—188°.

N-*Piperonylene-anthranilic acid,* $CH_2<{}^{O}_{O}>C_6H_3\cdot CH:N\cdot C_6H_4\cdot CO_2H$, after crystallisation from alcohol, forms yellow needles and prisms melting at 192—193°. It is sparingly soluble in toluene, but dissolves in ammonia yielding a colourless solution.

N-p-*Aminobenzylidene-anthranilic acid,*

$$NH_2\cdot C_6H_4\cdot CH:N\cdot C_6H_4\cdot CO_2H,$$

crystallises from alcohol in dark red prisms, melting and decomposing at 225—227°. Its solution in ammonia is colourless.

N-p-*Nitrobenzylidene-anthranilic acid* crystallises from alcohol in colourless plates melting at 165—167°. J. J. S.

Preparation of Nitriles. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 157617).—Schiff's bases, and also the polymolecular condensation products from aromatic amino-compounds and aliphatic or aromatic aldehydes, react on warming with a dilute solution of hydrocyanic acid in water or dilute alcohol to form nitriles of the general formula NHR·CHR'·CN, where R is an aromatic group, and R' hydrogen or an alkyl or aryl group. The temperature of reaction varies in different cases, closed vessels being employed to avoid loss of hydrocyanic acid. Thus, the anhydro-base from *p*-toluidine and formaldehyde yields *ω-cyanomethyl-*p*-toluidine,* melting at 62°, and in the same way *ω-cyano-*o*-chlorobenzylaniline,* melting at 77°, *ω-cyanobenzylanthranilic acid,* melting at 175°, and *ω-cyanoethylanthranilic acid,* melting at 192°, may be prepared.

Benzylidene-α-naphthylamine, from benzaldehyde and α-naphthylamine, melts at 73—74° and yields *ω-cyanobenzyl-α-naphthylamine,* melting at 116—117°, with hydrocyanic acid. In similar manner, benzylidene-β-naphthylamine yields *ω-cyanobenzyl-β-naphthylamine,* melting at 115°. C. H. D.

Preparation of Nitriles. HANS BUCHERER (D.R.-P. 157710, 157840, 157909, and 157910. Compare Abstr., 1902, i, 533; 1903, i, 612, and preceding abstract).—Ketones react with derivatives of aromatic amines of acid reaction and metallic cyanides to form nitriles in presence of an indifferent solvent. The amine salt must be capable of setting free hydrogen cyanide, at the same time losing its acid reaction. Thus acetone, aniline hydrochloride, and potassium cyanide react together in moist ether to form the nitrile,

$$NHPh\cdot CH_2\cdot CHMe\cdot CN$$

(Tiemann, Abstr., 1883, 199). The reaction takes place in light petroleum solution without the addition of water. Benzaldehyde and formaldehyde react in the same manner as acetone.

The sodium hydrogen sulphite compounds of Schiff's bases of the naphthalene series, like the corresponding benzene compounds, yield nitriles with potassium cyanide.

ω-Cyanomethyl-β-naphthylamine, from the sodium hydrogen sulphite compound of anhydroformaldehyde-β-naphthylamine, melts at 105°.

It is also possible to prepare nitriles of the same type without isolation of the Schiff's bases, avoiding the presence of an excess of sulphurous acid, which gives rise to loss of hydrogen cyanide (compare

Eibner, Abstr., 1901, i, 376). Thus, molecular quantities of formaldehyde, sodium hydrogen sulphite, and aniline are warmed at 90°. After a few minutes, potassium cyanide is added and ω-cyanomethylaniline immediately separates. In the case of β-naphthylamine, some naphthacridine is formed, and is removed by filtration before the addition of potassium cyanide.

Acetaldehyde reacts in the same way as formaldehyde and benzaldehyde.

Details of the preparation of several nitriles are given.

C. H. D.

Introduction of Carboxyl Groups into Phenol by the Action of Carbon Dioxide. I. Salicylic Acid. S. Tijmstra, jun. (*Ber.*, 1905, **38**, 1375—1385).—The immediate product obtained by heating sodium phenoxide with carbon dioxide at 120—130° under pressure is o-*sodoxybenzoic acid* (*sodium phenoxide*-o-*carboxylic acid*), $ONa \cdot C_6H_4 \cdot CO_2H$, and is not identical with sodium salicylate. This is shown by its having a considerably greater dissociation tension than sodium salicylate by the fact that, unlike the latter, it slowly absorbs dry ammonia gas at the ordinary temperature and by its violently decomposing with evolution of carbon dioxide when thrown into petroleum at 170—180°, whereas sodium salicylate requires a temperature of 230° to produce the same effect. The compound

$$ONa \cdot C_6H_4 \cdot CO_2H$$

is not transformed into sodium salicylate by boiling with water and evaporating to dryness or by being heated alone in a sealed tube for 4 hours at 248°; on the other hand, it is completely converted into this salt by dissolution in acetone. *o*-Sodoxybenzoic acid, when heated with methyl iodide during 2 days at 140—150°, gives methyl salicylate, although pure sodium salicylate under the same conditions is not changed, but the presence of a little disodium salicylate enables sodium salicylate also to interact with methyl iodide, giving methyl salicylate. The formation of this ester from *o*-sodoxybenzoic acid is probably due to the transformation of the *o*-methoxybenzoic acid originally formed under the influence of *o*-sodoxybenzoic acid; it is shown that a trace of the latter is sufficient to convert *o*-methoxybenzoic acid, when heated at 140—150° for 24 hours, into its isomeride. Sodium salicylate, when heated for $2\frac{1}{2}$ hours in a sealed tube at 248°, undergoes a more or less complete change into *o*-sodoxybenzoic acid.

The foregoing facts show that in the production of salicylic acid by Kolbe's synthesis the carbon dioxide directly enters the nucleus; contrary to the usually accepted view, sodium phenyl carbonate cannot play any essential part in the synthesis, as it completely decomposes into its constituents at a temperature of 85°. The peculiar transformation of *o*-sodoxybenzoic acid in acetone solution and its stability in presence of water are discussed at some length. W. A. D.

Brominated *cyclo*Propanedicarboxylic Acids. Eduard Buchner and Wilhelm Wedemann (*Ber.*, 1905, **38**, 1599—1602. Compare Buchner, Abstr., 1895, i, 269).—When heated with bromine and red

phosphorus in a sealed tube at 150—160° for 6—8 hours, *cis-* or *trans-cyclo*propane-1 : 2-dicarboxylic acid yields two isomeric dibromo-derivatives.

*α-Dibromo*cyclo*propane*-1 : 2-*dicarboxylic acid*, $C_5H_4O_4Br_2$, crystallises in small, colourless prisms, and when rapidly heated becomes grey at 220°, darkens at 275°, and melts and decomposes at 282°. It is only slightly soluble in chloroform, but dissolves readily in ether or alcohol, and is stable towards alkaline permanganate.

*β-Dibromo*cyclo*propane*-1 : 2-*dicarboxylic acid* crystallises in small, colourless, glistening prisms, melts at 202°, is more soluble than the α-isomeride in water or organic solvents, and does not decolorise alkaline permanganate solution.

When reduced with sodium amalgam in aqueous solution, both dibromo-acids yield *trans-cyclo*propane-1 : 2-dicarboxylic acid. G. Y.

Constitution of the Phthalein Salts. RICHARD MEYER and OSKAR SPENGLER (*Ber.*, 1905, **38**, 1318—1333).—A reply is given to Green and Perkin's criticisms (Trans., 1904, **85**, 398) of a previous paper (Abstr., 1903, i, 833), the lactonoid structure for quinolphthalein salts being still maintained. When phenolphthalein is digested with an excess of *N*-sodium hydroxide solution, the salt which is dissolved has the composition $C_{20}H_{12}O_4Na_2$; similarly, quinolphthalein and phenolphthalein anilide behave as dibasic acids, giving respectively the salts $C_{20}H_{10}O_5Na_2$ and $C_{20}H_{12}O_3Na_2$:NPh. These facts point to phenolphthalein having in its red alkaline solutions the same lactonoid structure which quinolphthalein and phenolphthalein anilide are admitted to have because they give colourless solutions with alkalis. Attempts were made to obtain evidence of the formation of a coloured quinonoid ether by methylating the alkali salts of phenolphthalein or quinolphthalein; but whether the methylation is effected by methyl iodide or methyl sulphate, in aqueous or alcoholic solution, with an excess of alkali or with sodium methoxide, the ordinary colourless, lactonoid dialkyl ethers of the type $\begin{matrix}C_6H_4\\ \vert\\ CO\cdot O\end{matrix}\!\!>C(C_6H_4\cdot OMe)_2$ are obtained. The normal sodium salts of the phthaleins give, on methylation, however, in addition to the dialkyl ethers, colourless, mono-alkyl ethers having the formulæ $\begin{matrix}C_6H_4\\ \vert\\ CO\cdot O\end{matrix}\!\!>C(C_6H_4\cdot OH)\cdot C_6H_4\cdot OMe$ and $\begin{matrix}C_6H_4\\ \vert\\ CO\cdot O\end{matrix}\!\!>C\!<\!\begin{matrix}C_6H_3(OMe)\\ C_6H_3(OH)\end{matrix}\!\!>O$ respectively; these substances form red alkali salts similar to those of the parent phthaleins. As the quinonoid formula for the phthaleins contains one carboxyl and one hydroxyl group, and the lactonoid formula two phenolic hydroxyl groups, the behaviour of benzoic acid and of phenol when methylated under the same conditions as the phthaleins was studied. Phenol is converted under all conditions, using methyl iodide or methyl sulphate in neutral, acid or alkaline solution, into its methyl ether; benzoic acid, on the other hand, gives rise to its ester only in acid solution, and not in presence of alkali even when methyl sulphate is employed. It is difficult to reconcile these facts with the quinonoid formula for the phthaleins.

It is considered that the formation of the colourless carbinol salt, $CO_2K\cdot C_6H_4\cdot C(OH)(C_6H_4\cdot OH)_2$, of phenolphthalein (Green and Perkin, *loc. cit.*) does not support the quinonoid formula for the coloured phthalein salts; it may be produced equally well by the following stages:

$$\text{I. } \begin{array}{l}C_6H_4\\ |\\ CO\cdot O\end{array}\!\!>C<\!\!\begin{array}{l}C_6H_4\cdot OK\\ C_6H_4\cdot OK\end{array} \longrightarrow \text{ II. } CO_2K\cdot C_6H_4\cdot C(OH)<\!\!\begin{array}{l}C_6H_4\cdot OK\\ C_6H_4\cdot OK\end{array} \longrightarrow$$
$$\text{III. } CO_2K\cdot C_6H_4\cdot C(OH)(C_6H_4\cdot OH)_2.$$

The coloured solution contains the salt I, which is transformed into the salt II by an excess of alkali; on adding acetic acid until the solution is neutral, the colourless salt III is formed.

Attempts to oxidise the ester, $CO_2Et\cdot C_6H_4\cdot CH<\!\!\begin{array}{l}C_6H_3(OH)\\ C_6H_3(OH)\end{array}\!\!>O$, derived from quinolphthalein, by means of potassium ferricyanide in slightly alkaline solution, to a true quinonoid derivative failed.

The coloured β-oxime of quinolphthalein decomposes barium carbonate, forming the *barium* salt, $(C_{20}H_{12}O_5N)_2Ba,2H_2O$, which crystallises in small, yellow nodules. The *barium* salt of the isomeric γ-oxime forms aggregates of small, yellow needles and is anhydrous. On boiling the β-oxime in alcoholic solution with dilute sulphuric acid during several days, it is transformed into the γ-oxime. It is probable that the two oximes have the structure $\begin{array}{l}C_6H_4\\ |\\ C{-}O\\ \|\\ N\cdot OH\end{array}\!\!>C<\!\!\begin{array}{l}C_6H_3(OH)\\ C_6H_3(OH)\end{array}\!\!>O$ and $\begin{array}{l}C_6H_4\\ |\\ C{-}O\\ \|\\ OH\cdot N\end{array}\!\!>C<\!\!\begin{array}{l}C_6H_3(OH)\\ C_6H_3(OH)\end{array}\!\!>O.$

W. A. D.

γ-Nitropropylphthalimide. SIEGMUND GABRIEL (*Ber.*, 1905, 38, 1692—1693).—*γ-Nitropropylphthalimide*,

$$C_8H_4O_2{:}N\cdot CH_2\cdot CH_2\cdot CH_2\cdot NO_2,$$

obtained by heating γ-iodopropylphthalimide with a mixture of silver nitrite, sea-sand, and absolute ether at 100°, crystallises from alcohol in glistening needles, melts at 83—84°, and may be distilled under reduced pressure.

When hydrolysed at 130—140° with concentrated hydrochloric acid, it yields phthalic acid, hydroxylamine, and a small amount of β-alanine.

J. J. S.

Reduction Products of Di-*p*-nitrobenzylmalononitrile. GIOVANNI ROMEO and C. MARCHESE (*Gazzetta*, 1905, 35, i, 121—131).—*Di-*p*-aminobenzylmalononitrile*, $C(CH_2\cdot C_6H_4\cdot NH_2)_2(CN)_2$, prepared by reducing di-*p*-nitrobenzylmalononitrile with tin and hydrochloric acid, separates from benzene in crystals melting at 161—163° and from alcohol in needles which contain $1C_2H_6O$ and melt at 159—161°; it is slightly soluble in water. Its *hydrochloride*, $C_{17}H_{16}N_4,2HCl$, is precipitated in the form of small needles melting at above 300°, and is very readily soluble in water and slightly so in hydrochloric acid. The *platinichloride*, $C_{17}H_{16}N_4,H_2PtCl_6,2H_2O$, forms a yellow, crystalline precipitate; it is reduced when heated in water or alcohol, and burns

without melting when heated on platinum. The *mercurichloride* forms aggregates of needles and melts and decomposes at 204—206°.

Dichlorodi-p-*aminodibenzylmalononitrile*, $C(CH_2{\cdot}C_6H_3Cl{\cdot}NH_2)_2(CN)_2$, occasionally formed along with di-*p*-aminobenzylmalononitrile on reducing di-*p*-nitrobenzylmalononitrile with tin and hydrochloric acid, crystallises from alcohol or xylene in starry aggregates of small needles melting at 200—201°, and dissolves in hydrochloric acid giving an unstable hydrochloride.

Di-p-*acetylaminobenzylmalononitrile* crystallises from alcohol or aqueous acetic acid in silvery scales melting at 258—260°.

Tetrabromodi-p-*aminodibenzylmalononitrile*,

$$C(CH_2{\cdot}C_6H_2Br_2{\cdot}NH_2)_2(CN)_2,$$

crystallises from benzene or xylene in tufts of white needles melting at 279—281° and decomposing at 285°, and is insoluble in acids owing to the presence of bromine in the molecule.

Tetrabromodi-p-*acetylaminodibenzylmalononitrile* crystallises from alcohol in small needles melting at 205—206°, and is soluble in benzene. When heated with an aqueous alcoholic solution of sodium hydroxide, it yields ammonia and *tetrabromodi*-p-*aminodibenzylcyanoacetic acid*, $CO_2H{\cdot}C(CN)(CH_2{\cdot}C_6H_2Br_2{\cdot}NH_2)_2$, which separates from alcohol in badly-defined crystals melting at 238°, and is moderately soluble in acetic acid and slightly so in xylene; it is a weak acid which dissolves readily in alkali hydroxide solutions, but with difficulty in alkali carbonate solutions. Its *amide*, prepared by reducing di-*p*-aminobenzylmalononitrile with sodium in alcoholic solution, crystallises from alcohol in slender needles melting at 231°. T. H. P.

Derivatives of the Iodobenzaldehydes containing Uni- and Ter-valent Iodine. By Conrad Willgerodt and Reinhold Rieke (*Ber.*, 1905, **38**, 1478—1486. Compare Patterson, *Diss.*, 1896).—The *semicarbazones* of *o*-, *m*-, and *p*-iodobenzaldehydes crystallise in colourless needles and melt respectively at 206°, 225—226°, and 224·5°. The *iodobenzylideneazines*, $C_6H_4I{\cdot}CH{<}\genfrac{}{}{0pt}{}{N}{N}{>}CH{\cdot}C_6H_4I$, obtained by the action of hydrazine sulphate on the iodoaldehydes, crystallise in yellow needles and melt at 184·5°, 146·5°, and 231° respectively. The *iodobenzylidene-benzidines*, $C_{12}H_8(N{:}CH{\cdot}C_6H_4I)_2$, form golden-yellow plates and melt at 252—253°, 235°, and above 360°.

Iodinium compounds have been obtained from the *m*- and *p*-iodoaldehydes, but not from the ortho-compound. These compounds were prepared by Meyer and Hartmann's method, and also by Willgerodt's method from the dichlorides and mercury diphenyl.

Salts of *benzaldehydephenyliodinium hydroxide*:

	Meta.	m. p.	*Para.*	m. p.
Chloride	Colourless needles	167°	Colourless prisms	183°
Bromide	,,	165	,, needles	157
Iodide	,,	142	,,	143
Nitrate	,,	163 dec.	—	—
Pyrochromate	Yellow needles	dec.	Yellow crystals	151 dec.
Platinichloride	Prisms	169 dec.	Yellow prisms	180 dec.
Mercurichloride	Colourless	dec.	Colourless crystals	172 dec.

A number of condensation products of *m*- and *p*-benzaldehydephenyliodinium iodides have been obtained:

	Meta.	m. p.	*Para.*	m. p.
Semicarbazone	Colourless prisms	204°	Colourless needles	212°
Phenylhydrazone ...	Yellow crystals	156	Yellow crystals	144
Benzidine compound	Yellow plates	228—229	Yellow plates	above 360

J. J. S.

Condensation of Aldehydes with Ketones. Edmund O. von Lippmann and Rodolfo Fritsch (*Ber.*, 1905, **38**, 1626—1630).—*Stilbeneacetone* (1 : 2-*diphenyl*-Δ^1-cyclo*pentene*-4-*one*), $CO<\begin{matrix}CH_2\cdot CPh\\ CH_2\cdot CPh\end{matrix}$, obtained by the condensation of benzaldehyde and acetone by means of zinc chloride, separates from a mixture of alcohol and ether as a yellowish-brown, crystalline precipitate softening at 167°, and is readily soluble in ether, chloroform, carbon disulphide, benzene, toluene, ethyl acetate, or acetic acid. When heated, 3 mols. of stilbeneacetone condense, with loss of $2H_2O$, to form *tristilbeneacetone-anhydride*, $C_{51}H_{38}O$, which can be more readily obtained by heating the original mixture of benzaldehyde, acetone, and zinc chloride for 10 hours at 200°, and separates from acetic acid in crystals melting at 188°, and is moderately soluble in ether, acetone, or chloroform.

Dipropylstilbeneacetone, $CO<\begin{matrix}CH_2\cdot C\cdot C_6H_4Pr\\ CH_2\cdot C\cdot C_6H_4Pr\end{matrix}$, prepared by the action of cuminaldehyde on acetone in presence of zinc chloride, separates from a mixture of chloroform and alcohol in pale yellow crystals melting at 158°, and is readily soluble in ether, chloroform, benzene, toluene, or ethyl acetate.

Dihydroxystilbeneacetone anhydride, $CO<\begin{matrix}CH_2\cdot C\cdot C_6H_4\\ CH_2\cdot C\cdot C_6H_4\end{matrix}>O$, prepared by the condensation of salicylaldehyde with acetone in presence of zinc chloride, melts at 215° and is soluble in most solvents except light petroleum.

Dimethoxystilbeneacetone, $CO<\begin{matrix}CH_2\cdot C\cdot C_6H_4\cdot OMe\\ CH_2\cdot C\cdot C_6H_4\cdot OMe\end{matrix}$, prepared from anisaldehyde and acetone, separates in pale brown crystals melting at 129°, and dissolves in the same solvents as the preceding compound.

Distyrylethyleneacetone, $CO<\begin{matrix}CH_2\cdot C\cdot CH:CHPh\\ CH_2\cdot C\cdot CH:CHPh\end{matrix}$, obtained by the condensation of cinnamaldehyde with acetone in presence of zinc chloride, separates from a mixture of benzene and light petroleum in yellowish-brown crystals melting at 208°. T. H. P.

Preparation of *cyclo*Hexanol, *cyclo*Hexanone, and Derivatives. Arnold F. Holleman, F. H. van der Laan, and H. J. Slijper (*Rec. trav. chim.*, 1905, **24**, 19—24. Compare Abstr., 1904, i, 40).—The crude product obtained by passing dry hydrogen, impregnated with phenol vapour, over reduced nickel heated at 140—150° contains

water, *cyclo*hexene, *cyclo*hexanol, and *cyclo*hexanone. The two former may be isolated by fractional distillation. From the residue, *cyclo*hexanone may be removed by the addition of sodium hydrogen sulphite, or more completely by conversion into dibenzylidene*cyclo*hexanone by the action of benzaldehyde in presence of sodium hydroxide, leaving *cyclo*hexanol, which may be purified by desiccation over lime and distillation; it boils at 159—160°, solidifies when cooled, and melts at 20°.

Sabatier and Senderens' method (Abstr., 1904, i, 156) of preparing *cyclo*hexanone from the mixture by passing the vapour over copper heated to 330° results in the production of *cyclo*hexene, *cyclo*hexane, and benzene, and a better yield of the ketone is obtained when the copper is heated to 280° and the vapour is mixed with a small quantity of air. The preparation of adipic acid and of *cyclo*pentanone (Hentzschel and Wislicenus, Abstr., 1893, i, 555) from the mixture of *cyclo*hexanol and *cyclo*hexanone is described. T. A. H.

Ketens. Hermann Staudinger (*Ber.*, 1905, **38**, 1735—1739).—*Diphenylketen*, $CPh_2:CO$, the first representative of a new type of compound, is prepared by the action of zinc on an ethereal solution of diphenylchloroacetyl chloride; it boils at 146° under 12 mm. pressure, has the colour of a concentrated solution of potassium dichromate, and solidifies in a freezing mixture to a mass of yellow crystals. It can be preserved in an atmosphere of carbon dioxide for weeks. On exposure to the atmosphere, it becomes viscid, and when light petroleum is added, a white insoluble oxidation product separates, which is also formed when a current of air is passed into the solution of the keten in benzene. Diphenylketen is vigorously acted on by water with the formation of diphenylacetic acid in quantitative yield. With ethyl alcohol, it forms ethyl diphenylacetate. It bears a further resemblance to carbimides in being acted on by primary bases, the *anilide* melting at 180°. The *amide* melts at 165° and the *phenylhydrazide* at 166—167°.

When a current of dry hydrogen chloride is passed into a solution of diphenylketen in benzene, diphenylacetyl chloride, boiling at 170—171° under 16 mm. pressure and melting at 55°, is obtained. When hydrogen chloride, containing traces of water, is passed into an ethereal solution of diphenylketen containing zinc chloride, ethyl diphenylacetate is formed.

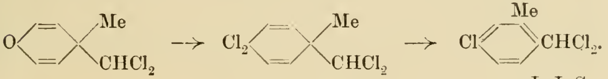
The keten is much more stable towards water in benzene solution than in ethereal solution. When a benzene solution of the keten is agitated with dilute hydrochloric acid, *diphenylacetic anhydride* is formed. It boils at 220—225° under 15 mm. pressure and separates from ether in needles which melt at 98°.

The unsaturated character of diphenylketen is further indicated by its power of combining with bromine, hydrogen sulphide, and ethyl sodiomalonate.

Phenylchloroacetyl chloride in ethereal solution was acted on by zinc dust. Phenylketen was not isolated from this reaction, but its existence was proved by the formation of phenylacetic acid on the addition of water. A. McK.

Cyclic Ketones from Chloroform and Phenols. KARL AUWERS and GUSTAV KEIL (*Ber.*, 1905, **38**, 1693—1697. Compare Abstr., 1902, i, 218; 1903, i, 100, 620; 1904, i, 26).—When 4-keto-1-methyl-1-dichloromethyldihydrobenzene (Abstr., 1902, i, 218) dissolved in light petroleum and mixed with an equivalent of phosphorus pentachloride at the ordinary temperature and the petroleum and oxychloride removed under reduced pressure, a chlorinated product is obtained which, on reduction with sodium and boiling alcohol, yields *o*-xylene. When the crude chlorinated product is heated with water at 160—180°, all the chlorine is removed from the side chain and p-*chloro*-o-*tolualdehyde*, $C_6H_3MeCl\cdot CHO$, is formed. It distils at 228°, has a sp. gr. 1·277 at 17°/17°, and solidifies to colourless crystals. Its *semicarbazone* crystallises in colourless needles and melts at 224°. On oxidation, the aldehyde yields Claus' *p*-chloro-*o*-toluic acid melting at 169—170° (Claus gives 172°).

The action of the pentachloride may thus be represented:



J. J. S.

Intramolecular Atomic Migrations. III. Benzopinacones. P. J. MONTAGNE (*Rec. Trav. chim.*, 1905, **24**, 105—131).—The principal results recorded in this paper have already been published (Abstr., 1902, i, 472, and this vol., i, 58). Linnemann's method (*Annalen*, 1865, **133**, 6) was employed for the reduction of 4 : 4′-dichlorobenzophenone to dichlorodiphenylcarbinol; the *acetyl* derivative of the latter melts at 43·5°. 4 : 4′ : 4″ : 4‴-Tetrachlorobenzopinacone, prepared from dichlorobenzophenone by Ciamician and Silber's method (Abstr., 1901, i, 36), forms molecular combinations with methyl alcohol (2 mols.), benzene (1 mol.), and toluene (1 mol.), melts at 147·5°, and decomposes at the same time into dichlorodiphenylcarbinol and dichlorobenzophenone; boiling with acetic acid induces the same decomposition.

4 : 4′ : 4″ : 4‴-Tetrachlorobenzopinacolin, prepared from the foregoing by Zagumenny's method (Abstr., 1877, i, 459; 1881, 813), melts at 194°, and on boiling with alcoholic potassium hydroxide yields tri-*p*-chlorophenylmethane and *p*-chlorobenzoic acid. The former melts at 92° and crystallises from light petroleum in short, thick, transparent, rhombic prisms [$a : b : c = 0·5904 : 1 : 0·9261$], which soon become opaque. The optical characters of the crystals were determined by Jaeger and are given in detail in the original.

Tri-*p*-nitrophenylcarbinol, when recrystallised from benzene, melts at 193° and does not combine with the solvent (compare Gomberg, Abstr., 1904, i, 490; E. and O. Fischer, *ibid.*, 864, and O. Fischer and Schmidt, *Zeit. Farb. Text. Ind.*, 1904, **3**, 1). The crystals are monoclinic prisms [$a : b : c = 1·4825 : 1 : 2·9474$; $\beta = 54°12'$]. Tri-*p*-aminophenylmethane melts at 202·5° (Graebe, 180°, Bernthsen, 203°, and E. Fischer, 207°). The trichlorophenylmethane, prepared from this by diazotisation in presence of cuprous chloride, is identical with that prepared from tetrachlorobenzopinacolin. T. A. H.

Derivatives of Indandione. GIORGIO ERRERA and E. CASARDI (*Gazzetta*, 1905, **35**, i, 1—11. Compare Abstr., 1903, i, 265).—*Ethyl indandionemethenylacetoacetate*, $C_6H_4<{CO \atop CO}>CH\cdot CH:CAc\cdot CO_2Et$, formed by the condensation of indandione (1 mol.) with ethyl ethoxymethyleneacetoacetate (1 mol.) in presence of sodium carbonate, separates from benzene or a mixture of benzene and light petroleum in yellow needles, turning red in the air and melting at 117—118°; it is an unstable compound and dissolves readily in bases, yielding the corresponding salts, or in alcohol. With aqueous ammonia, it yields aminomethyleneindandione, whilst on heating with ammonium acetate and acetic acid it gives *a*-di-*o*-benzylenonepyridine.

Indandionemethenylacetone, $C_6H_4<{CO \atop CO}>CH\cdot CH:CHAc$, formed by boiling ethyl indandionemethenylacetoacetate with dilute alkali hydroxide solution and subsequently acidifying, crystallises from ethyl acetate in golden-yellow needles melting at 177—178° and dissolving slightly in the ordinary solvents; with bases, it yields red, crystalline salts. The mother liquor from the indandionemethenylacetone contains methenylbisindandione and another *compound* separating from acetic acid in golden-yellow needles melting at 267·5°.

The *anhydride of indandionemethenylacetonedioxime*,

$$\begin{array}{l} OH\cdot N:C\text{——}C:CH\cdot CH \\ \quad\;\; | \qquad\quad | \\ \quad C_6H_4\cdot C:N\text{——}O \end{array} \!\!>CMe \quad \text{or} \quad \begin{array}{l} OH\cdot N:C\text{——}C\cdot CH:CH \\ \quad\;\; | \qquad\quad | \\ \quad C_6H_4\cdot C\cdot O\text{——}N \end{array} \!\!>CMe,$$

prepared by boiling indandionemethenylacetone with excess of hydroxylamine hydrochloride in aqueous alcoholic solution, separates with $1H_2O$ from aqueous alcohol in yellow leaflets which melt and decompose at 246° and dissolve in solutions of bases.

The solution of indandionemethenylacetone in aqueous ammonia deposits brown or red crystals, $C_{13}H_{11}O_2N,2H_2O$, which melt and decompose at 240°, dissolve slightly in acetone and, when boiled with alkalis, yield ammonia and the original ketone. When boiled with concentrated acetic acid, this ammonia-derivative loses water and undergoes condensation, yielding 2-o-*benzylenone*-6-*methylpyridine* (2-*phenylene*-6-*methylpyridineketone*), according to the equation:

$$C_6H_4<{CO \atop CO}>C:CH\cdot CH:CMe\cdot NH_2 = H_2O + \begin{array}{l} CO\text{—}C:CH\cdot CH \\ \;|\qquad\; | \qquad\;\; || \\ C_6H_4\cdot C:N\text{—}CMe \end{array};$$

this compound crystallises from light petroleum in leaflets or flattened needles which melt at 121° and dissolve readily in alcohol or benzene. It is a feeble base, being precipitated from acetic acid solution by water; the *hydrochloride* crystallises in slender, yellow needles, slightly soluble in concentrated hydrochloric acid. It yields an *oxime*, $C_{13}H_{10}ON_2$, crystallising from alcohol in minute, yellowish-white scales, which melt at 256—257° and dissolve slightly in light petroleum and readily in xylene.

2-o-*Benzylene*-6-*methylpyridine*, $\begin{array}{l} CH_2\text{—}C:CH\cdot CH \\ \;|\qquad\; | \qquad\;\; || \\ C_6H_4\cdot C:N\text{—}CMe \end{array}$, obtained by reducing the corresponding ketone by means of hydriodic acid and phosphorus, is deposited as a *hydrate* (with $2H_2O$) in the form of shining, white needles which melt at 45—48° to a turbid liquid and at

100° to a clear liquid; the crystals lose their water of crystallisation in a vacuum over potassium hydroxide, yielding anhydrous, hexagonal crystals of the formula $C_{13}H_{11}N$, which have a faintly aromatic odour and melt at 31—32° and boil with slight decomposition at 325°. The *hydrochloride*, $C_{13}H_{11}N,HCl$, crystallises in long, silvery needles, which melt at 282° and dissolve slightly in hydrochloric acid and moderately well in water. The *picrate*, $C_{13}H_{11}N,C_6H_3O_7N_3$, crystallises from alcohol in yellow needles melting at 211—212°. T. H. P.

Amino-derivatives of Anthraquinone. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 156803).—When a cooled solution of α-diazoanthraquinone sulphate is oxidised by an excess of sodium hypochlorite, yellow needles of the *sodium* salt of *anthraquinone-α-nitroamine*, $C_{14}H_7O_2\cdot NNa\cdot NO_2$, separate. When decomposed by dilute acids or carbon dioxide, the *nitroamine* is obtained, and crystallises from dilute acetic acid in yellow needles, melting and decomposing at 193°. It is insoluble in water, and dissolves sparingly in alcohol, acetone, or benzene. Fuming nitric acid converts it into 4-*nitroanthraquinone-α-nitroamine*, a light brown, crystalline powder, exploding at 117°. Sodium sulphide reduces it to 1 : 4-diaminoanthraquinone.

Anthraquinone-1 : 5-*dinitroamine*, $C_{14}H_6O_2(NH\cdot NO_2)_2$, prepared in similar manner, explodes at 203° and forms a golden-yellow *sodium* salt. Nitric acid converts it into 4 : 8-*dinitroanthraquinone*-1 : 5-*dinitroamine*, which explodes at 134°. Sodium sulphide reduces it to 1 : 4 : 5 : 8-tetra-aminoanthraquinone, characterised by the blue colour of its acetone solution. C. H. D.

Connection between the Constitution and the Colour and Dyeing Power with Mordants of the Hydroxyanthraquinones and their Sulphonic Acids. GEORG VON GEORGIEVICS (*Zeit. Farb. Text. Ind.*, 1905, **4**, 185—192. Compare Möhlau and Steimmig, *ibid.*, **3**, 273 and 358).—The fact that 3-hydroxyanthraquinone is a strong mordant dye is regarded as indicating the incompleteness of Möhlau and Steimmig's view that tinctorial properties in the anthraquinone series are produced by a hydroxyl group in the ortho-position. A simple rule connecting the dyeing properties and the constitution of these substances cannot be deduced. A hydroxyl group in position 3 in alizarin produces a far greater effect than the same group introduced into any other position in the molecule; anthragallol (1 : 2 : 3-trihydroxyanthraquinone) dyes brown shades, which may be regarded as produced by a combination of 1 : 3- and 2 : 3-dihydroxyanthraquinones. All other hydroxylated alizarins resemble the parent substance in giving red dyes. The influence on the colour of a hydroxyl group in position 5 or 8 is greater than that of the same group in position 6 or 7; moreover, the effect when in position 5 is greater than when in position 8. A hydroxyl group introduced into position 5 in quinizarin (1 : 4-dihydroxyanthraquinone), instead of increasing the dyeing power towards mordanted fabrics, diminishes it; the product behaves as a combination of 1 : 8- and 1 : 5-dihydroxyanthraquinones, these two substances possessing little tinctorial

properties towards mordants. Probably for a similar reason, 1 : 4 : 5 : 8-tetrahydroxyanthraquinone has little tinctorial value.

On sulphonation with sulphuric acid containing 20 per cent. of anhydride, dihydroxyanthraquinones containing both hydroxyl groups in the same nucleus give monosulphonic acids; when the two hydroxyls are heteronuclear, a disulphonic acid is obtained. The entrance of the sulphonic group, in all the cases studied, caused an intensification of the dyeing properties towards mordants.

Sodium quinizarinsulphonate, $C_{14}H_7O_4 \cdot SO_3Na, 2\frac{1}{2}H_2O$, crystallises in spherular aggregates of very slender needles or in thin plates. *Sodium xanthopurpurinsulphonate*, with $\frac{3}{4}H_2O$, forms hard, brown needles. *Sodium 1-hydroxyanthraquinonesulphonate* forms golden-yellow needles, and probably contains $1H_2O$; the isomeric *sodium 2-hydroxyanthraquinonesulphonate* crystallises from dilute alcohol in sheaves of needles containing $1H_2O$. *Sodium anthrarufin*-di-*sulphonate*,

$$C_{14}H_6O_4(SO_3Na)_2, 1\frac{1}{2}H_2O,$$

forms microscopic, prismatic crystals. The *sodium* salt of sulphoanthraflavic acid, $C_{14}H_6O_4(SO_3Na)_2$, seems to contain $3H_2O$.

W. A. D.

Action of Acetic Anhydride and Sodium Acetate on Phenanthraquinone. Wassili Scharwin (*Ber.*, 1905, **38**, 1270—1272).—When heated on a water-bath with sodium acetate and acetic anhydride, phenanthraquinone yields, as the principal product of the reaction, a *substance*, $C_{33}H_{22}O_7$, which crystallises in colourless, transparent, rhombic plates, becomes dark blue, and decomposes at about 250°; becomes yellow when exposed to light, and dissolves in concentrated sulphuric acid to an olive-green solution. When warmed with aqueous sodium hydroxide, it is converted into Meyer and Spengler's lactone, $C_{16}H_8O_3$ (this vol., i, 219). The action of phenylhydrazine on the substance $C_{33}H_{22}O_7$ leads to the formation of a *compound*, $C_{18}H_{12}O_3$, which crystallises in orange needles, melts and decomposes at 251°, and dissolves in concentrated sulphuric acid to a violet solution.

Along with the main product, phenanthraquinone yields small quantities of diacetylphenanthraquinol and of a *substance* which crystallises in opaque, glistening, bronze rhombohedra and dissolves in benzene, chloroform, or concentrated sulphuric acid to blue solutions, which become colourless when exposed to light. G. Y.

Dicamphorquinone and *iso*Dicamphorquinone. Giuseppe Oddo (*Gazzetta*, 1905, **35**, i, 12—27).—On the basis of Komppa's synthesis of camphor according to Bredt's formula, the author attributes to dicamphor the structural formula $C_8H_{14}<\begin{matrix}CH\cdot CH\\ | \quad\; | \\ CO \;\; CO\end{matrix}>C_8H_{14}$, and to dicamphorquinone and *iso*dicamphorquinone the formulæ

$$C_8H_{14}<\begin{matrix}C{=\!=}C\\ | \quad\; | \\ CO \;\; CO\end{matrix}>C_8H_{14} \text{ and } C_8H_{14}<\begin{matrix}C\text{———}C\\ \| \qquad\quad \| \\ C\cdot O\cdot O\cdot C\end{matrix}>C_8H_{14}$$

respectively.

Dicamphorquinone is partially or completely converted into the

isomeric *iso*dicamphorquinone by the action of hydrobromic acid, bromine, nitrosyl chloride, potassium permanganate, chromium trioxide, sodium peroxide, phosphorus pentachloride, nitrobenzene, or concentrated potassium hydroxide solution or by fusion with potassium hydroxide. The *iso*dicamphorquinone formed either remains unchanged or is but slightly attacked by the reagents named. In the above isomerisation, the author assumes the formation of intermediate unstable additive products according to the scheme:

$$C_8H_{14}<\begin{matrix}C{=}C\\ \vert\quad\vert\\ CO\ CO\end{matrix}>C_8H_{14} + HBr = C_8H_{14}<\begin{matrix}CBr{-}CH\\ \vert\qquad\vert\\ CO\quad CO\end{matrix}>C_8H_{14}.$$

The latter then splits up, giving either the original dicamphorquinone or its isomeride.

Only one such *additive compound*, $C_8H_{14}<\begin{matrix}CI{-}C(OH)\\ \vert\qquad\vert\\ CO\quad CO\end{matrix}>C_8H_{14}$, was obtained, and was prepared by the action of yellow mercuric oxide (2 mols.) and iodine (2 mols.) on dicamphorquinone (1 mol.) in alcohol. It crystallises from benzene in small, dark red, shining scales melting at 142—145°, and is converted into dicamphorquinone by aqueous sulphurous acid, and into camphorquinone by boiling its alcoholic solution with yellow mercuric oxide until decolorised.

Fusion of dicamphorquinone with potassium hydroxide yields, besides *iso*dicamphorquinone, *camphenonecamphenoic acid*,

$$C_8H_{14}<\begin{matrix}CH{=\!=}C\\ \qquad\ \vert\\ CO_2H\ \ CO\end{matrix}>C_8H_{14},$$

which is also obtained in small quantity when *iso*dicamphorquinone is fused with potassium hydroxide.

When boiled for a long time with nitric acid, dicamphorquinone is converted into camphoric anhydride and camphoric acid, whilst under the same conditions *iso*dicamphorquinone is almost completely changed, but yields no definite products.

The action of sodium or magnesium on $\beta\beta$-dibromocamphor in toluene solution yields dicamphor, resinous substances, and dicamphorquinone. In ethereal solution, magnesium and $\beta\beta$-dibromocamphor give the compound $C_8H_{14}<\begin{matrix}CBr{\cdot}MgBr\\ \vert\\ CO\end{matrix}, \frac{1}{2}Et_2O$. T. H. P.

Carvone. Hans Rupe and Paul Schlochoff (*Ber.*, 1905, 38, 1719—1725).—A 55 per cent. yield of 8-*hydroxy*-8 : 9-*dihydrocarvone*, $CMe<\begin{matrix}CH{\cdot}CH_2\\ CO{-}CH_2\end{matrix}>CH{\cdot}CMe_2{\cdot}OH$, is obtained when carvone is shaken for 70 hours with 10 times its weight of 40 per cent. sulphuric acid. It distils at 154° under 10 mm. pressure, solidifies on cooling, and melts at 41—42°. It is readily soluble in water and organic solvents, has a sp. gr. 0·8282 at 20° and $[\alpha]_D$ +43·06° at 20°. The *oxime*, $C_{10}H_{17}O_2N$, crystallises in colourless needles melting at 114—114·5° and sparingly soluble in water. The *semicarbazone*, $C_{11}H_{19}O_2N_3$, crystallises from dilute alcohol in flat needles and melts at 176°. When reduced, the dihydrocarvone yields 2 : 8-dihydroxyterpane, which is identical with Baeyer's glycol (Abstr., 1895, i, 550) melting at 112—113°.

When dihydrocarveol is shaken with 35 per cent. sulphuric acid

during 48 hours, the product is a mixture of Baeyer's glycol, α-2 : 8-dihydroxyterpane, and a stereoisomeride, β-2 : 8-*dihydroxyterpane.* A better yield of the latter is obtained by shaking with 40 per cent. acid during 90 hours. It is less soluble in benzene than the α-compound, crystallises in slender, colourless needles, melts at 103—104°, and combines with sulphuric acid more readily than the stereoisomeride. Its sp. gr. is 0·8273 at 20° and it has $[\alpha]_D$ +12·61° at 20°.

When an acetone solution of the crude dihydroxyterpane is slowly added to boiling 25 per cent. sulphuric acid through which steam is being passed, a mixture of dihydropinol, terpenes, dihydrocarveol, and cymene is obtained. The *dihydropinol,*

$$CH\begin{cases} CH_2—CH——CMe_2 \\ \quad\quad\quad >CH_2 \mid \\ CHMe\cdot CH——O \end{cases},$$

is most readily isolated as its *ferricyanide,* which is then decomposed by sodium carbonate. The oxide distils at 58·5° under 9 mm. pressure, has a sp. gr. 0·9192 at 20° and $[\alpha]_D$ +34·97° at 20°, and closely resembles cineol. J. J. S.

Terpenes and Ethereal Oils. Constitution of Eucarvone and its Reduction Products. OTTO WALLACH [with HUGO KÖHLER] (*Annalen,* 1905, 339, 94—116).—The formula $\begin{matrix} CMe\cdot CO\cdot CH \\ \| \quad\quad\quad | \\ CH\cdot CH_2\cdot CH \end{matrix}>CMe_2$, proposed by Baeyer for eucarvone, is not in accord with many of the reactions discovered by that investigator, and still less with other recent observations.

By reducing eucarvone, Baeyer only obtained the unsaturated dihydroeucarveol, $C_{10}H_{17}\cdot OH$, but it has been found that at the same time 14—20 per cent. of the saturated tetrahydroeucarveol, $C_{10}H_{19}\cdot OH$, is also formed. Further, pure eucarvoxime yields tetrahydroeucarvylamine, together with the saturated ketone, $C_{10}H_{18}O$, as by-product. Baeyer has shown that the tetrahydrocarvone has a seven-membered ring, $\begin{matrix} CHMe\cdot CO\cdot CH_2 \\ | \\ CH_2—CH_2\cdot CH_2 \end{matrix}>CMe_2$, and, further, the saturated ketone, $C_{10}H_{18}O$, obtained by direct reduction of eucarvone, yields the *keto-acid,*

$$COMe\cdot[CH_2]_3\cdot CMe_2\cdot CH_2\cdot CO_2H,$$

which can be converted into $\beta\beta$-dimethylpimelic acid,

$$CO_2H\cdot[CH_2]_3\cdot CMe_2\cdot CH_2\cdot CO_2H,$$

the latter giving 1 : 1′-dimethyl*cyclo*-3-hexanone, $\begin{matrix} CH_2\cdot CO—CH_2 \\ | \quad\quad\quad | \\ CH_2\cdot CH_2\cdot CMe_2 \end{matrix}$.

These facts suggest that eucarvone has a seven-membered ring, $\begin{matrix} CMe\cdot CO\cdot CH_2 \\ \| \\ CH—CH{:}CH \end{matrix}>CMe_2$. The oxamino-oxime of eucarvone yields, on reduction, an unsaturated diamine of which the phosphate on distillation gives not *m*-cymene, but *p*-cymene.

In the formation of eucarvone from the hydrobromide of carvone, it is suggested that under the influence of the alkali hydroxide the three-membered ring is broken, a hydrated compound being formed,

$$\begin{matrix} CMe\cdot CO——CH_2 \\ \| \\ CH\cdot CH_2\cdot CH(OH) \end{matrix}>CMe_2,$$

which then passes into eucarvone. It is uncertain what position the ethylene linking occupies in dihydrocucarvone; it is possible that in the reduction a rearrangement has taken place.

Eucarvone is prepared from carvone hydrobromide and methyl-alcoholic potassium hydroxide, and purified by conversion into the semicarbazone; it boils at 85—87° under 12 mm. pressure, has a sp. gr. 0·949 and $n_D = 1·5092$ at 21°, and is optically inactive. When reduced in absolute alcohol in moist ether, a mixture of dihydroeucarvone and an alcohol are obtained, which is oxidised with 10 per cent. potassium permanganate, the alcohol remaining unchanged. Tetrahydroeucarvone is prepared by oxidising the alcohol with chromic acid; it boils at 91—93° under 13 mm. and at 212—216° under the ordinary pressure, and has a sp. gr. 0·918 and $n_D = 1·4673$ at 22°; its oxime is a liquid, and its semicarbazone consists of a mixture of two compounds differing in solubility and melting at 161—163° and 191—192° respectively. On oxidation with chromic acid in the presence of sulphuric acid, it yields a keto-acid, which is a liquid solidifying in a freezing mixture and boiling at 194—196° under 39 mm. pressure; its *semicarbazone* melts at 170—171° and its *oxime* at 100—101°. When treated with sodium hypobromite, ββ-dimethyl-pimelic acid, melting at 102—103°, is obtained; its calcium salt, on distillation with soda lime, yields 1 : 1′-dimethyl-3-*cyclo*hexanone, which melts at 173—175° and gives a *semicarbazone* sintering at 192° and melting at 195°.

Tetrahydrocarveol is prepared by reducing the pure tetrahydroeucarvone, boils at 219—220°, and yields, with phenylcarbimide, a *phenylurethane* melting at 74—75°.

Tetrahydrocarvone can be converted into a ketonic acid and then into *iso*propyladipic acid (m. p. 75—76°), in the same manner as tetrahydroeucarvone.

Eucarvoxime yields a hygroscopic *hydrochloride*, $C_{10}H_{14}$:NOH,HCl, which is a snow-white powder melting at 68—70°; a hydrobromide melting and decomposing at 77—79°, and a hydriodide were also prepared. On reducing an alcoholic solution of the oxime by sodium, tetrahydroeucarvylamine is obtained; it is an oil boiling at 209—211°; its *benzoyl* derivative melts at 168°. K. J. P. O.

Ethereal Oil of Birch Buds. Hugo von Soden and Fritz Elze (*Ber.*, 1905, **38**, 1636—1638).—The essential oil of birch buds contains:

(1) A paraffin, which separates from methyl alcohol in odourless, tasteless needles melting at 50°, and is readily soluble in ether, benzene, or light petroleum. (2) An ester not yet investigated. (3) A primary sesquiterpene alcohol, $C_{15}H_{23}·OH$, to which the name *betulol* is given. It is a colourless, very viscous oil, with an odour resembling that of incense and a bitter taste. It has a sp. gr. 0·975 at 15°, $[\alpha]_D$ −35°, and boils at 138—140° under 4 mm., and, with partial decomposition, at 284—288° under 743 mm. pressure. It is soluble in 3 parts of 70 per cent. alcohol. *Betulol acetate*, $CH_3·CO_2·C_{15}H_{23}$, is a colourless, faintly aromatic smelling oil, which has the sp. gr. 0·986 at 15° and boils at

142—144° under 4 mm. pressure. The acid phthalate is obtained as a transparent resin showing no tendency to crystallise. T. H. P.

Gutta-percha from German New Guinea. Alexander Tschirch and O. Müller (*Arch. Pharm.*, 1905, **243**, 114—132. Compare Abstr., 1904, i, 76).—The sample examined was the product of *Palaquium supfianum*; the percentage of it soluble in water, alcohol, acetone, alcohol-chloroform, ether, and light petroleum respectively was 1, 12, 15, 34, 40, 40 at 17°, 2, 40, 42, 50, 96, 97 at the boiling temperature, whilst in benzene, toluene, chloroform, and carbon bisulphide 97 per cent. dissolved at both temperatures.

The material was extracted thoroughly with boiling water, then with boiling 96 per cent. alcohol. From the alcoholic extracts, alban crystallised, but consisted of three different crystalline forms; these were separated by digestion with 96 per cent. alcohol, first at 40°, then at 60°, and crystallisation until fractions were obtained with a uniform appearance under the microscope. *α-Guinalban* (needle-alban), $C_{42}H_{70}O$, crystallises in needles and melts at 171°; *β-guinalban* (crystal-alban), $C_{22}H_{32}O$, crystallises in lustrous plates and melts at 136°; *γ-guinalban* (spherite-alban), $(C_{22}H_{32}O)_4$ (molecular weight determined), crystallises in little spheres and melts at 111°. β- and γ-Guinalbans both yield cinnamic acid when boiled with alcoholic potassium hydroxide (compare van Romburgh, Abstr., 1904, 905); in addition, they yielded respectively *β-guinalbaresinol*, melting at 107°, and *γ-guinalbaresinol*, $C_{26}H_{44}O$, melting at 168°, both of which crystallise in needles. The amount of α-guinalban did not permit of a similar experiment being made with it; nor did the amount of β-guinalbaresinol permit of an analysis.

The mother liquor from the guinalban was poured into water acidified with hydrochloric acid, when guinafluavil was precipitated; by treatment with 80 per cent. alcohol, it was separated into an insoluble, α, and a soluble, β, portion, both yellow and amorphous. *α-Guinafluavil*, $(C_{22}H_{36}O)_3$ (molecular weight determined), melts at 83°, *β-guinafluavil*, $C_{15}H_{24}O$, at 78°; both yield cinnamic acid when boiled with alcoholic potassium hydroxide, and in addition respectively *α-guinafluaviloresinol*, $C_{28}H_{48}O_2$, which melts at 136°, and *β-guinafluaviloresinol*, which melts at 143°; these crystallise best from acetone. From some crude fluavil, a product was obtained by hydrolysis which separated from a solution in dilute alcohol, on slow evaporation of the solvent, in forms resembling in structure grains of potato starch; after crystallisation from acetone, it melted at 172°, and had the composition $C_{28}H_{48}O_2$.

The residue left after the extraction of the gutta-percha with alcohol was dissolved in chloroform and the solution was poured into alcohol; the precipitated albanan was crystallised from alcohol-chloroform. *Guinalbanan*, $C_{48}H_{88}O$, melts at 62° and takes up oxygen gradually from the air, especially when exposed to light.

The substance remaining in solution when the albanan was precipitated was purified by repeated solution in chloroform and precipitation with alcohol. This substance, *guinagutta*, $C_{10}H_{16}$, separates from a hot ethereal solution, on cooling, as an apparently amorphous, white

mass, which under the microscope is seen to contain curved needles; at 60°, it shrinks to a glassy mass; alcoholic potassium hydroxide does not act on it; when exposed to the air it turns red.

The colour reactions of a number of these substances are tabulated and compared with those of phytosterol, which they resemble in many respects.

In all, 500 grams of the gutta-percha were worked up. From 300 grams, the yield of crude alban was 86 grams, of crude fluavil 25 grams. The weights of pure albans obtained were α, 0·3; β, 2·5; γ, 10·0 grams; of albanan, about 2 grams.

It will be noticed that the terms alban, fluavil, albanan, and gutta are used as generic names, a syllable being prefixed to them to indicate the material from which particular varieties of them are derived. When several substances have the same name, that distinguished as α has the highest melting point, that called β the next highest, &c.

C. F. B.

The Albans and Fluavil of Sumatra Gutta-percha. ALEXANDER TSCHIRCH and O. MÜLLER (*Arch. Pharm.*, 1905, **243**, 133—140. Compare Abstr., 1904, i, 76, and preceding abstract for the nomenclature). —α-Sumalban (crystal-alban), from old gutta-percha, is hydrolysed by 10 per cent. alcoholic potassium hydroxide to cinnamic acid and crystalline *α-sumalbaresinol*, $C_{52}H_{84}O_2$ or $C_{50}H_{80}O_2$, which melts at 207°. β-Sumalban (spherite-alban), from old gutta-percha and from a commercial sample, yields cinnamic acid and crystalline *β-sumalbaresinol*, $C_{50}H_{80}O_2$ or $C_{48}H_{76}O_2$ (molecular weight determined), which melts at 151°. γ-Sumalban (*iso*spherite-alban), from commercial gutta-percha, yields cinnamic acid and crystalline *γ-sumalbaresinol*, $C_{40}H_{64}O_2$, which melts at 171°.

Fluavil from old gutta-percha yields cinnamic acid when hydrolysed with alcoholic potassium hydroxide, but the resinol also formed could not be made to crystallise either from acetone or from dilute alcohol. Fluavil from commercial gutta-percha is not decomposed.

Sumagutta, both from old and from commercial gutta-percha, is not attacked by alcoholic potassium hydroxide.

The colour reactions of these substances were compared with those of phytosterol, and are tabulated in the paper. C. F. B.

Albans of Mikindani-caoutchouc from German East Africa. ALEXANDER TSCHIRCH and O. MÜLLER (*Arch. Pharm.*, 1905, **243**, 141—146).—The variety of india-rubber from Mikindani in German East Africa, known as Mozambique Balls, contains a certain amount of resin, and this was investigated for comparison with the resins of gutta-percha. The sample was boiled with water and then extracted thoroughly with acetone. From the solution, a crude alban crystallised; the mother liquor, when evaporated, left a yellow, sticky mass easily soluble in cold alcohol, with a few crystals of the alban, of which 3·5 grams in all were obtained from 1000 of the rubber. The crude material melted at 168—172°, and was seen under the microscope to consist of two substances; it was separated into these by treatment

with 96 per cent. alcohol at 60°. Of the more soluble portion, *α-danialban*, $C_6H_{12}O$, 0·9 gram was obtained; it crystallises in spherites, melts at 178°, and is not stable in the air. The yield of the less soluble portion, *β-danialban*, $C_{30}H_{48}O$, was 1 gram; it crystallises in plates and melts at 149°. Neither of these substances yields cinnamic acid when heated with alcoholic potassium hydroxide, differing in this respect from the albans obtained from gutta-percha.

Several colour reactions of these substances are tabulated; in these, the substances much resemble phytosterol. C. F. B.

A White Peru Balsam. [C. Hartwich and] A. Hellström (*Arch. Pharm.*, 1905, **243**, 218—237. Compare Thoms and Biltz, Abstr., 1904, i, 1038).—The sample examined came from Honduras, and was a cloudy, yellow, syrupy liquid having a sp. gr. 1·089, $\alpha_D + 7°20'$, n_D 1·5925 at 20°, acid number 27, saponification number 165; 94 per cent. of it dissolved in alcohol, and it contained 75 per cent. of cinnamein (aromatic esters).

The portion insoluble in alcohol consisted of *honduresen*, $C_{64}H_{64}O_{10}$, a white, amorphous substance which melts at 310—315° and is very inert chemically, but is decomposed by fusion with potassium hydroxide with formation of benzoic acid and a brown resin.

The alcoholic solution of the balsam was evaporated, and the residue dissolved in ether. When the ethereal solution was shaken with 5 per cent. aqueous sodium carbonate, a sticky substance separated which crystallises from alcohol; this is a sodium derivative of *honduresinol*, $C_{16}H_{26}O_2$, which itself is amorphous, melts at 286°, gives colour reactions resembling those of cholesterol, and in general much resembles benzoresinol and storesinol (Tschirch, Abstr., 1893, i, 480; 1902, i, 109). The sodium carbonate solution was found to have taken up much cinnamic acid.

The ethereal solution was then extracted with 1 per cent. aqueous potassium hydroxide. By salting out the extract with concentrated aqueous sodium hydroxide, a product was obtained which can be crystallised from alcohol; this is the salt of a substance, itself amorphous, which melts at 156—161°, has the composition $C_{16}H_{26}O_2$, and appears to be identical with styresinol (Tschirch, Abstr., 1902, i, 110). A little more of this is precipitated when the alkaline solution is acidified, together with much cinnamic acid and *honduresinotannol*, $C_{40}H_{45}O_{10}$, which is brown and amorphous, begins to shrink together at 300°, forms an amorphous *acetyl* derivative melting at 215°, and in its reactions resembles siaresinotannol (Ludy, Abstr., 1893, i, 666).

The ethereal solution was then shaken with aqueous sodium hydrogen sulphite, but no aldehyde or ketone could be isolated.

The ethereal solution now remaining was evaporated and the residue distilled with steam. The non-volatile portion was hydrolysed with concentrated sodium hydroxide solution; the products were cinnamic alcohol, phenylpropyl alcohol, cinnamic acid, and a little styresinol. The volatile portion consisted of phenylpropyl alcohol and a *terpene*, $C_{10}H_{16}$, which boiled at 261—262° and took up 2 atoms of bromine in acetic acid solution. C. F. B.

Solanin from Solanum sodomæum. GIUSEPPE ODDO and AMEDEO COLOMBANO (*Gazzetta*, 1905, **35**, i, 27—45).—The widely varying data given by different authors concerning solanin are probably to be explained by the fact that the various solanins obtained from different sources are not one and the same product. It is also possible that, at different stages of their growth, the plants contain compounds of analogous behaviour, but different compositions.

The authors have used various methods for the extraction of solanin from *Solanum sodomæum*, the most convenient consisting of prolonged maceration (5 months) with 91 per cent. alcohol, the filtered extract being then treated with 1 per cent. acetic acid solution and subsequently with lime-water; on boiling the precipitate thus obtained with 80 per cent. alcohol in a current of carbon dioxide, a yield of 0·266 per cent. of solanin is obtained. Its composition is $2C_{23}H_{39}O_8N,H_2O$, the water being lost on drying at 105°, and it crystallises from 80 per cent. alcohol in flocculent aggregates of slender, white needles, which turn brown at 230° and melt and decompose at 245—250°, and when powdered form microscopic, transparent scales. It is very slightly soluble in absolute alcohol, and gelatinises in 90 per cent. alcohol; it dissolves slightly in acetone, and more so in methyl alcohol, which deposits crystals melting at 275—280°. Its principal reactions are as follows: when a small quantity is treated with a drop of cold concentrated sulphuric acid, it becomes first yellow and then deep red, afterwards slowly changing to violet and brown; the coloration is more intense with the product crystallised from methyl alcohol. The solution in concentrated nitric acid is colourless at first, but changes to pale yellow, which deepens after a time. A drop of a hot mixture of absolute alcohol and sulphuric acid does not impart the green colour to the crystals described by Cazeneuve and Breteau (Abstr., 1899, i, 551), but after a time the liquid assumes a pale rose-red colour; with this same reagent, a sample of solanin from commercial *Solanum tuberosum* gave a pale violet coloration, the liquid becoming rose-red. With the double iodide of bismuth and potassium, it gives a dark yellow precipitate, becoming paler on standing. Phosphomolybdic acid gives a greenish-white precipitate, and the Froehde-Buckingham reagent yields first a yellow coloration which reddens and turns brown after a few minutes. The best reaction is that of Missaghi (*Gazzetta*, 1875, **5**, 417), which is, however, also given by solanidin. It consists in adding one or two drops of dilute platinic chloride solution to a few drops of solanine solution in a watch-glass, and evaporating on a water-bath at 65—70° until almost dry; a red coloration then appears, which changes to intense purple and becomes violet if the heating is continued; the colour slowly disappears if the heating is stopped, but it returns when the glass is again put on the bath. If an alcoholic solution of solanin is slowly evaporated on a water-bath with a solution of platinic iodide and potassium iodide, a yellow coloration appears which becomes red and finally violet with green layers, more especially when cold.

Solanin hydrochloride, $C_{23}H_{39}O_8N,HCl$, separates from a mixture of alcohol and ether in shining, microscopic scales which begin to blacken at about 135°, do not melt at 265°, and are soluble in water. The

aurichloride forms a yellow, crystalline precipitate which is soluble in alcohol, begins to blacken at 115° and decomposes at 122°. The *platinichloride* forms a crystalline powder somewhat soluble in water.

Solanin evidently contains an amino-group in the aromatic nucleus, since with nitrous acid and β-naphthol it apparently becomes converted into an oxyazo-compound, which functions as an indicator, being turned red by acids and yellow by alkalis.

When boiled with 2 per cent. hydrochloric acid, solanin undergoes hydrolysis to solanidin, $C_{19}H_{29}ON$, which crystallises from aqueous alcohol in small, nacreous scales melting at 190—192°, and dissolves in ether and, to a slight extent, in acetone or light petroleum. Its alcoholic solution has a faintly alkaline reaction, and it forms difficultly soluble salts. It can be diazotised and with β-naphthol gives a product which behaves towards acids and alkalis similarly to the corresponding product obtained from solanin. Besides solanidin, the hydrolysis of solanin by hydrochloric acid yields a dextrorotatory hexose, giving an osazone, $C_{18}H_{22}O_4N_4$, which melts and decomposes at 186°. T. H. P.

Solanin. JOHANN WITTMANN (*Monatsh.*, 1905, **26**, 445—467. Compare Firbas, Abstr., 1890, 75; Schulz, Abstr., 1901, i, 92; Hilger and Merkens, Abstr., 1903, i, 847; Zeisel and Wittmann, Abstr., 1904, i, 80; Votoček and Vondráček, Abstr., 1904, i, 177).—Firbas' formulæ for solanin, $C_{52}H_{93}O_{18}N$, and for solanidin, $C_{40}H_{61}O_2N$, are confirmed by analysis, and, for the latter, by molecular weight determinations by the boiling point method. The sugar obtained by hydrolysis of solanin contains galactose, rhamnose, and a sugar or mixture of sugars which has $[\alpha]_D + 33{\cdot}65°$, yields an osazone which melts at 198—200°, and is probably a polysaccharide. The presence of dextrose could not be determined with certainty. G. Y.

Caryophyllin. HANS MEYER and OTTO HÖNIGSCHMID (*Monatsh.*, 1905, **26**, 379—389).—Caryophyllin is obtained from the buds of *Caryophyllus aromaticus* by digestion with alcohol at the laboratory temperature for 14 days, or by extraction with ether and removal of resinous impurities by treatment of the product with aqueous sodium hydroxide or ammonia. It crystallises from alcohol in clusters of long, slender, silky needles, melts at 295°, sublimes without decomposition in a vacuum, is without odour or taste, and gives Liebermann's cholesterol reaction. The *tetra-acetyl* derivative, $C_{40}H_{60}O_4Ac_4$, crystallises in slender, colourless needles, commences to soften at 245°, and melts at 268—271°. Caryophyllic acid, $C_{40}H_{64}O_{12}$ or $C_{40}H_{62}O_{12}$, formed by treatment of caryophyllin with fuming nitric acid (compare Mylius, *Ber.*, 1873, **6**, 1053), crystallises in colourless needles, which become red on exposure to direct sunlight, and forms amorphous, yellow salts. The *methyl* ester, $C_{40}H_{60}O_8(OMe)_4$, formed by the action of diazomethane on the acid in ethereal solution, or of methyl iodide on the silver salt, crystallises in slender, colourless needles and melts at 164—165°. When boiled with sodium acetate and acetic anhydride, the acid forms an *acetyl* derivative, which crystallises in slender, colourless needles, melts at 200—204°, and decomposes at 206°.

The action of diazomethane on caryophyllin leads to the formation of the *methyl* ether, $C_{40}H_{63}O_3{\cdot}OMe$, which melts at 187° and forms a *triacetyl* derivative, $OMe{\cdot}C_{40}H_{60}(OAc)_3$. This crystallises in broad, glistening needles and melts at 212—213°. G. Y.

Influence of Active Groups in the Textile Fibres on the Process of Dyeing. WILHELM SUIDA (*Monatsh.*, 1905, **26**, 413—427. Compare this vol., i, 75).—The action of acylating or of alkylating reagents on cotton-wool produces no change in its behaviour towards pararosaniline, crystal-violet, bordeaux extra, or azopararosaniline. When shaken with benzoyl chloride and aqueous sodium hydroxide, cotton-wool acts as a catalytic agent, accelerating the formation of benzoic acid and sodium chloride. Pararosaniline solution, after decolorisation with cotton-wool, gives a strong chlorine reaction, showing the salt to have been dissociated in the process of dyeing. It is probable that, owing to the slightly active nature of the hydroxyl groups in cellulose, the dyeing of cotton-wool is a physical process.

Wool and silk, which are aminocarboxylic acids, are dyed, in the neutral bath, an intense red by pararosaniline, intense violet by crystal-violet, and a weak red by azopararosaniline. After treatment with acetyl chloride, acetic anhydride, or absolute alcohol and sulphuric acid, wool and silk are only slightly coloured by pararosaniline or crystal-violet, but are dyed an intense red by azopararosaniline. The microscopic appearance of the wool or silk fibres is not altered by acetylation or alkylation; after hydrolysis with aqueous ammonium carbonate, the fibres give the same reaction as untreated wool or silk to the three dyes in question. Wool or silk fibres which have been treated with benzoyl chloride and aqueous sodium hydroxide are partially dyed, whilst fibres which have been boiled with ethyl bromide, which results probably in ethylation of the amino-, but not of the carboxyl-, groups, are dyed the normal colours. G. Y.

Pyrone. II. RICHARD WILLSTÄTTER and RUDOLF PUMMERER (*Ber.*, 1905, **38**, 1461—1472. Compare Abstr., 1904, i, 1043; Collie, Trans., 1904, **85**, 971).—When warmed for a short time with dilute alkalis, pyrone is transformed into derivatives of bishydroxymethyleneacetone, $CO(CH{:}CH{\cdot}OH)_2$. With aqueous potassium hydroxide, the dipotassium derivative is formed, and with potassium methoxide the methyl potassium derivative, $OK{\cdot}CH{:}CH{\cdot}CO{\cdot}CH{:}CH{\cdot}OMe$, which was previously described as an additive compound of pyrone and potassium methoxide. The monopotassium derivative, when heated with methyl iodide and methyl alcohol, yields the *dimethyl ether*, $CO(CH{:}CH{\cdot}OMe)_2$, in the form of an oil distilling at 138—142° under 13·5—14 mm. pressure. Its alcoholic solution is neutral, gives only a faint pink coloration with ferric chloride, and is soluble in water. Pyrone, 3-methylpyrone, and an *oil*, $C_8H_{14}O_3$, boiling at 75—81° under 10 mm. or at 191—194° (corr.) under atmospheric pressure are formed during the methylation.

The addition of an ethereal solution of hydrogen chloride to the monopotassium derivative yields the free *monomethyl ether*,

$$OH{\cdot}CH{:}CH{\cdot}CO{\cdot}CH{:}CH{\cdot}OMe,$$

as a yellow oil with acid properties; it gives a deep red coloration with ferric chloride, and is readily transformed into pyrone. The potassium compound gives precipitates with silver nitrate, mercuric chloride, mercurous nitrate, and cupric chloride. The *cupric* salt, $(C_6H_7O_3)_2Cu$, crystallises from ethyl acetate in glistening, greyish-green prisms melting at 157—158°.

The *benzoate*, OBz·CH:CH·CO·CH:CH·OH, obtained by carefully hydrolysing the methyl benzoate (m. p. 98·5—99°) previously described, crystallises from light petroleum in yellow plates melting at 80·5—81°. It has an acid reaction, gives a coloration with ferric chloride, and is readily hydrolysed. When dissolved in sodium carbonate solution and immediately precipitated with sulphuric acid, a second modification is obtained. This also melts at 81°, but is less soluble in light petroleum and crystallises differently. The *copper* derivative, $(C_{12}H_9O_4)_2Cu$, crystallises in long, soft, green prisms and decomposes at 200°.

The *dibenzoate*, $CO(CH:CH·OBz)_2$, obtained by shaking a solution of pyrone in sodium hydroxide with benzoyl chloride or by further benzoylating the monobenzoyl compound, separates from alcohol in colourless prisms, melts at 111·5—112°, and gives a red coloration with ferric chloride after a time or on heating. An alcoholic solution of pyrone containing hydrogen chloride readily reacts with ethyl orthoformate, even at the ordinary temperature, yielding the *hexaethylacetal* of diformylacetone, $C(OEt)_2[CH_2·CH(OEt)_2]_2$. This is due to the rupture of the pyrone ring, a rupture which occurs much more readily in the pyrone than in the furan series. The acetal is colourless, distils at 279—282° (corr.), has a sp. gr. 0·982 at 0°/4°, and is only sparingly soluble in cold water. When shaken with twenty times its weight of 1 per cent. hydrochloric acid, it is hydrolysed to *bishydroxymethyleneacetone*, which has been isolated as the *copper* derivative, $C_5H_4O_3Cu$. Pyrone is obtained when the monomethyl ether is distilled, or the monobenzoate is heated at its melting point or boiled with light petroleum (b. p. 100—140°). The benzoate of the methyl ether and the mono- and di-benzoates of the hydroxy-compound are quantitatively converted into pyrone by ethereal hydrogen chloride.

3-*Methylpyrone* distils at 108—113° under 11 mm. pressure, crystallises from light petroleum in prisms, melts at 66·5—67·2°, dissolves readily in water, ethyl alcohol, ethyl acetate, or benzene, and yields precipitates with ethereal solutions of hydrogen chloride, oxalic or prussic acids, but no precipitate with an alcoholic solution of calcium chloride.

Some of these reactions are used as arguments against Collie's formulæ for pyrone derivatives. J. J. S.

Action of Bromine on Ethyl Dimethylpyronedicarboxylate. F. Carlo Palazzo (*Chem. Centr.*, 1905, i, 1258—1259; from *Giorn. Sci. Nat. Econ.*, **25**, 207—216. Compare Abstr., 1904, i, 762).—By the action of bromine on ethyl dimethylpyronedicarboxylate, a dibromo-derivative, $O<\begin{matrix}C(CH_2Br):C(CO_2Et)\\C(CH_2Br):C(CO_2Et)\end{matrix}>CO$, and a tetrabromo-derivative, $O<\begin{matrix}C(CHBr_2):C(CO_2Et)\\C(CHBr_2):C(CO_2Et)\end{matrix}>CO$, are formed together with a liquid. The

constitution of the bromo-derivatives has been proved by their synthetical formation by the action of carbon oxychloride on the copper salt of ethyl γ-monobromoacetoacetate (compare Epprecht, Abstr., 1894, i, 171). Conrad and Guthzeit's ester behaves with bromine, therefore, in a similar manner to other derivatives of 1 : 4-pyrone, which also form substitution products, although the molecule contains double linkings. The constitution of the ester may therefore be represented by the formula $O<\begin{matrix}CMe{:}C(CO_2Et)\\CMe{:}C(CO_2Et)\end{matrix}>CO$. The formation of malonic acid by the action of barium hydroxide on the ester (Abstr., 1891, 672) is explained by assuming that ethyl acetonedicarboxylate, $CO(CH_2{\cdot}CO_2Et)_2$, is formed as an intermediate product. Since the compound $C_7H_9O_4N$ is also obtained by the action of hydroxylamine in solutions which are not alkaline, the action is really one of hydrolysis.

The bromine derivatives of ethyl dimethylpyronedicarboxylate are prepared by adding a solution of bromine in carbon disulphide to a solution of the ester in the same solvent. The *dibromo*-derivative crystallises from alcohol in colourless plates, melts at 126°, and is soluble in dilute acetic acid, acetone, alcohol, ethyl acetate, benzene or chloroform, sparingly so in ether or light petroleum, but almost insoluble in water.

The *tetrabromo*-derivative, obtained by evaporating the carbon disulphide mother liquor, crystallises from dilute acetic acid or carbon disulphide in octahedra, melts at 142°, and is readily soluble in acetone, benzene, or chloroform, less so in alcohol or acetic acid, and insoluble in water or light petroleum. A fluorescent solution is formed by adding a few drops of ammonia to a solution of the tetrabromo-derivative in acetone. An intensely yellow solution is formed by adding an alkali to an alcoholic solution, and potassium permanganate is instantly reduced. Both bromo-derivatives yield hydrogen bromide, carbon dioxide, acetone, and alcohol when boiled with an aqueous solution of an alkali, and both on reduction with zinc and acetic acid form ethyl dimethylpyronedicarboxylate; the latter was identified by converting it into ethyl lutidonedicarboxylate (Abstr., 1887, i, 502).

E. W. W.

3 : 5-Diacetyl-2 : 6-dimethylpyrone and the Constitution of the Synthetical γ-Pyrone Compounds. F. Carlo Palazzo and P. Onorato (*Chem. Centr.*, 1905, i, 1259—1260; from *Giorn. Sci. Nat. Econ.*, **25**, 217—238. Compare preceding abstract).—Whilst accepting Collie's formula for diacetyldimethyl-γ-pyrone (Trans., 1904, 971; compare also Thomas and Lefèvre, Abstr., 1889, i, 235), the authors point out the impossibility of dividing the pyrones into two classes according to their basic properties. The varying basicity of the pyrones is more probably due to the influence of the substituting groups in accordance with Willstätter and Pummerer's theory of the constitution of pyrones (Abstr., 1904, i, 1043).

3 : 5-Diacetyl-2 : 6-dimethylpyrone, $O<\begin{matrix}CMe{:}CAc\\CMe{:}CAc\end{matrix}>CO$, crystallises from alcohol in long, lustrous needles, melts at 124—125°, and is

soluble in light petroleum, ether, carbon disulphide, acetic acid, benzene, toluene, chloroform, or acetone, but only sparingly so in water; it sublimes in a vacuum without decomposing. When boiled with a 5 per cent. solution of barium hydroxide, it is decomposed, forming carbon dioxide, acetone, and acetic acid, and by the action of an alcoholic solution of ammonia it yields 3 : 5-diacetyl-2 : 6-dimethylpyridone, $\mathrm{NH}{<}{\substack{\mathrm{CMe{:}CAc}\\ \mathrm{CMe{:}CAc}}}{>}\mathrm{CO}$, which crystallises from ethyl acetate in white, lustrous needles and melts at 232°. The *anhydride of a dioxime*, $\mathrm{O}{<}{\substack{\mathrm{CMe{:}C{\cdot}CMe{:}N} \\ {>}\mathrm{CO} \\ \mathrm{CMe{:}C{\cdot}CMe{:}N}}}{>}\mathrm{O}$, formed by the action of hydroxylamine on diacetyldimethylpyrone, crystallises from light petroleum and melts at 68°. The yellow substance, formed by the action of light on the compound $C_{11}H_{12}O_4$, appears to be merely another form of the same compound. Solutions of the yellow compound in benzene, toluene, chloroform, carbon disulphide, or ether are yellow. The colourless alcoholic solution requires a comparatively long exposure to sunlight before it becomes yellow. The yellow solutions gradually become colourless in diffused light. E. W. W.

Action of Carbonyl Chloride on the Copper Derivative of Benzoylacetone and on Dithiobenzoylacetone. VICTOR VAILLANT (*Bull. Soc. chim.*, 1905, [iii], **33**, 458—460. Compare Abstr., 1896, i, 591, and Feist, Abstr., 1891, 459).—When dithiobenzoylacetone, dissolved in benzene, or the copper derivative of benzoylacetone, suspended in benzene, is treated with carbonyl chloride dissolved in toluene, 3 : 5-*diacetyl*-2 : 6-*diphenylpyrone*, $\mathrm{O}{<}{\substack{\mathrm{PhC{:}CAc}\\ \mathrm{PhC{:}CAc}}}{>}\mathrm{CO}$, is formed, which crystallises from boiling alcohol in colourless needles, sinters at 175°, melts at 178—180°, is readily soluble in chloroform or benzene, and gives a red coloration with solution of ferric chloride after some hours, indicating that it is hydrolysed by this reagent into a β-diketonic substance. T. A. H.

4′-Hydroxyflavonol. ANNA EDELSTEIN and STANISLAUS VON KOSTANECKI (*Ber.*, 1905, **38**, 1507—1509. Compare Gutzeit and Kostanecki, this vol., i, 366).—4′-*Methoxyflavanone*,

$$\mathrm{C_6H_4}{<}{\substack{\mathrm{O{-}CH{\cdot}C_6H_4{\cdot}OMe} \\ \mathrm{CO{\cdot}CH_2}}},$$

prepared by boiling an alcoholic solution of 2′-hydroxy-4-methoxychalkone with dilute sulphuric acid, crystallises from alcohol in plates and melts at 97°.

3-iso*Nitroso*-4′-*methoxyflavanone*, $C_{16}H_{13}O_4N$, prepared from methoxyflavonone, amyl nitrite, and hydrochloric acid, separates from dilute alcohol as a yellow, crystalline powder and, when boiled with dilute mineral acids, forms 4′-*methoxyflavonol*, $\mathrm{C_6H_4}{<}{\substack{\mathrm{O{-}C{\cdot}C_6H_4{\cdot}OMe} \\ \mathrm{CO{\cdot}C{\cdot}OH}}}$, which separates from alcohol in pale yellow, glistening needles and melts at 225°. The latter compound produces a bright yellow shade

with aluminium mordants; it forms a yellow *sodium* salt and dissolves in concentrated sulphuric acid to a fluorescent solution; its *acetyl* derivative separates from dilute alcohol in colourless needles and melts at 138—139°. When 4'-methoxyflavonol is boiled with hydriodic acid, it forms 4'-*hydroxyflavonol*, $C_6H_4<\begin{matrix}O-C\cdot C_6H_4\cdot OH \\ CO\cdot \overset{||}{C}\cdot OH\end{matrix}$, which separates from alcohol in yellow needles and melts at 276°. Its solutions in dilute aqueous sodium hydroxide and in concentrated sulphuric acid respectively are fluorescent, whilst it yields a yellow shade with aluminium mordants; its *diacetyl* derivative melts at 158°.

A. McK.

Phenothioxins. FERDINAND MAUTHNER (*Ber.*, 1905, **38**, 1411—1415).—1 : 3-*Dinitrophenothioxin*, $C_6H_4<\begin{matrix}O\\S\end{matrix}>C_6H_2(NO_2)_2$, prepared by the reduction of *o*-dihydroxydiphenyl disulphide with sodium amalgam to thiocatechol and subsequent condensation of this with picryl chloride in alcoholic solution, crystallises in orange-red plates melting at 187°; it dissolves in concentrated sulphuric acid to a red solution. 1 : 3-*Diaminophenothioxin*, prepared by reducing the dinitro-compound with tin and hydrochloric acid, crystallises in colourless needles melting at 158°; the *sulphate* forms colourless needles. 1 : 3-*Diacetyldiaminophenothioxin* separates from alcohol in colourless needles melting at 224—225°; 1 : 3-*dibenzoyl diaminophenoxthin* melts at 257°.

1 : 3-*Dinitrophenothioxin oxide*, $C_6H_4<\begin{matrix}O\\SO\end{matrix}>C_6H_2(NO_2)_2$, prepared by oxidation with dilute nitric acid, crystallises in yellow needles, melts at 202—203°, and dissolves in concentrated sulphuric acid to a blood-red solution.

1 : 3-*Dinitrophenothioxin dioxide*, $C_6H_4<\begin{matrix}O\\SO_2\end{matrix}>C_6H_2(NO_2)_2$, formed on oxidising dinitrophenoxthin with chromic acid, crystallises from benzene in pale yellow needles melting at 256·5—257°. Stannous chloride reduces it to 1 : 3-*diaminodiphenothioxin dioxide*, which crystallises in colourless needles and melts at 228°.

E. F. A.

Formation of Inactive Arginine. E. PROVAN CATHCART (*Proc. Physiol. Soc.*, 1905, xxxix—xl; *J. Physiol.*, **32**).—The conditions usually associated with racemisation phenomena, namely, high temperature and powerful reagents, are more nearly realised in the case of acid than in enzyme hydrolysis, yet it is the latter which (in some cases) yields the racemic arginine. This is more remarkable in view of the belief that an enzyme molecule is asymmetric. Some suggestions are offered as explanations, and experiments are being continued.

W. D. H.

Salts of the Hexone Bases with Picrolonic Acid. HERMANN STEUDEL (*Zeit. physiol. Chem.*, 1905, **44**, 157—158).—Arginine picrolonate has the composition $C_{16}H_{22}O_7N_8$, that is, it is formed by the union of 1 mol. of base with one of acid, and not with two, as pre-

viously stated (Abstr., 1903, i, 431). Histidine picrolonate has the composition $C_{10}H_8O_5N_4,C_6H_9O_2N_3$. Details of the preparation of picrolonic acid are given. J. J. S.

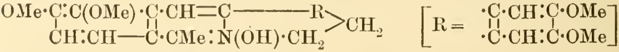
Corydalis Alkaloids. Johannes Gadamer (*Arch. Pharm.*, 1905, **243**, 147—154).—In part an introduction to the following abstracts; in part physiological (see this vol., ii, 411). C. F. B.

Alkaloids of the Subaerial Parts of Corydalis cava and Corydalis solida. Otto Haars (*Arch. Pharm.*, 1905, **243**, 154—165).—From the leaves and stems of both of these plants, gathered at the flowering season, bulbocapnine was isolated; with the first of them the yield was 0·6 per cent. of the dried drug. From 18 kilos. of dried *Corydalis cava* there were also obtained 1·5 grams of a new *alkaloid*, $C_{21}H_{21}O_8N$; this melts at 230°; unlike the other corydalis alkaloids it is lævorotatory, having $[\alpha]_D - 112·8°$ at 20°; it was found to be a monacid base, the *platinichloride*, which melts at 214°, being analysed; it is insoluble in alkali hydroxides, and it contains no methoxyl groups.

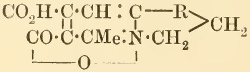
Out of the alcoholic mother liquor, from which the alkaloids just mentioned had been obtained, 0·5 gram of another new *alkaloid*, $C_{21}H_{23}O_7N$ or $C_{21}H_{25}O_7N$, was isolated; this melts at 137·5°, has $[\alpha]_D + 96·8°$ at 20°, and exhibits triboluminescence; it contains two OMe and one NMe groups.

Protopine could not be detected. C. F. B.

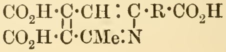
Constitution of Corydaline. Otto Haars (*Arch. Pharm.*, 1905, **243**, 165—197. Compare Dobbie and Lauder, Trans., 1897, **71**, 657; 1902, **81**, 145, &c.).—The author has repeated much of the work of Dobbie and Lauder, and obtained substantially the same results. A few discrepancies and additional observations are detailed below; some of these lead to the following formulæ, which differ slightly from those of Dobbie and Lauder:



Dehydrocorydaline.



Corydic Acid.



Corydilic Acid.

Dehydrocorydaline in solution is a quaternary ammonium base. In the free state it melts and decomposes at 112—113°, has the composition $C_{22}H_{25}O_5N$, and must be regarded as a ψ-base with the keto-composition, containing the groups ·CMeO and NH< instead of ·CMe:N(OH)<, for it forms an *oxime* (compare Gadamer, this vol., i, 368), $C_{22}H_{26}O_5N_2$, which melts and decomposes at 165°, and it condenses with *p*-aminodimethylaniline yielding the product, $C_{30}H_{35}O_4N_3$, which melts at 120—130°.

An attempt to resolve the optically inactive corydaline melting at 135° (Gadamer, Abstr., 1902, i, 307) into its active constituents was unsuccessful. Yet probably this substance should be regarded as *r*-corydaline, each active constituent of which has either both asymmetric carbon atoms *d*, or both *l*. The inactive corydaline melting at 158° has been separated partially into its active constituents, and neither of these is identical with the active corydaline that occurs naturally; probably this inactive variety should be regarded as *r*-mesocorydaline, in the two active constituents of which the two asymmetric carbon atoms are respectively $d:l$ and $l:d$.

Corydic acid, $C_{18}H_{17}O_6N$, was obtained crystallised with $1H_2O$ in transparent rhombohedra, melting at 224°, and with $2H_2O$ in yellow needles, melting at 218°. It is to be regarded as a betaine-acid, for it reacts like a monobasic acid with aqueous potassium hydroxide, and, when heated with methyl-alcoholic potassium hydroxide and methyl iodide, it forms the *iodide* of the *dimethyl ester*, $C_{20}H_{22}O_6NI,4H_2O$, which has the character of a quaternary ammonium iodide. This salt melts at 100°; the corresponding *chloride*, with $4H_2O$, *platinichloride*, with $2H_2O$, and *aurichloride*, the last melting at 145°, were also analysed. *Ethyl corydate hydriodide* was also prepared; it melts at 112°.

Corydilic acid, $C_{17}H_{15}O_8N$, was obtained crystallised with $2H_2O$. It has the character of a tertiary base; for, when it is heated with methyl-alcoholic potassium hydroxide and methyl iodide, it forms *trimethyl corydilate methiodide*, $C_{21}H_{24}O_8NI$, which melts at 142°; the corresponding *nitrate* melts at 102°.

Corydaldine crystallises in the monoclinic system [$a:b:c = 1{\cdot}6181:1:2{\cdot}7827$; $\beta = 125°52'$]. C. F. B.

Pilocarpine. VI. Adolf Pinner (*Ber.*, 1905, 38, 1510—1531. Compare Abstr., 1901, i, 340; 1902, i, 232, 638).—Now that it has been established that pilocarpine is a glyoxaline derivative with the probable constitution $\begin{matrix} CHEt\cdot CH\cdot CH_2\cdot C\cdot NMe \\ | \qquad\quad | \qquad\qquad \| \\ CO{-}O\cdot CH_2 \qquad CH{-}N \end{matrix}\!\!>\!CH$, the author has studied the constitution of certain derivatives of pilocarpine and of *iso*pilocarpine.

When the requisite amount of sulphuric acid is added to barium pilocarpoate, and the aqueous solution, after removal of the barium sulphate, is concentrated, a syrup is obtained, on the addition of alcohol to which the *substance* $C_{11}H_{14}O_4N_2$ is formed; it crystallises in glistening prisms, melts at 180°, and has acid properties. When heated at 200—210°, it forms iso*pilocarpoic acid*, $C_{11}H_{16}O_5N_2$, which crystallises in needles and melts at 150°. *Ethyl* iso*pilocarpoate*, $C_{11}H_{14}Et_2O_5N_2$, prepared by the esterification of pilocarpoic acid or of *iso*pilocarpoic acid with ethyl alcohol, is an oil; its *hydrochloride* forms deliquescent crystals; its *platinichloride* melts at 200°. When pilocarpoic acid is heated for 10 hours at 100° with potassium hydroxide and an excess of ethyl bromide, a mixture of ethyl *iso*-pilocarpoate and its ethobromide is formed, the *platinichloride*,

$$(C_{11}H_{14}Et_2O_5N_2,EtBr)_2PtCl_4,$$

of the latter compound melting at 107° and decomposing at about 190°.

By the oxidation of pilocarpoic acid with potassium permanganate, α-ethyltricarballylic acid, $C_8H_{12}O_6$, melting at 145—146°, is formed, and not pilomalic acid, $C_7H_{12}O_5$, as previously described by the author. The α-ethyltricarballylic acid thus prepared is optically active, whilst Jowett's acid, prepared by fusion of homopilopic acid with potassium hydroxide, is optically inactive and melts at 157° (Trans., 1901, **79**, 1331). The author confirms Jowett's observations on the behaviour of the calcium salt (Trans., 1901, **79**, 1344). When the crude ester, prepared from the acid, alcoholic potassium hydroxide, and ethyl bromide, is heated at 100° for 72 hours with methyl alcohol and ammonia, *α-ethyltricarballylic triamide*, $C_8H_9O_3(NH_2)_3$, crystallising in needles, is formed; it begins to decompose at 265°.

By the action of ethyl alcohol on the crude acid chloride, obtained by the action of phosphorus oxychloride on α-ethyltricarballylic acid, a mixture of the tri-, di-, and mono-ethyl esters is formed, the latter preponderating.

Bromocarpic acid, $C_{10}H_{15}O_4N_2Br$, dissolves in a warm concentrated aqueous solution of barium hydroxide, and is reprecipitated when this solution is acidified. When heated with barium hydroxide solution for 8 to 10 hours at 130°, ammonia, methylamine, barium carbonate, and barium pilomalate are produced, but not barium oxalate; the action is represented as follows: $C_{10}H_{15}O_4N_2Br_2 + 2O + 3H_2O = HBr + 3CO_2 + NH_3 + CH_3{\cdot}NH_2 + C_7H_{12}O_5$.

When dibromo*iso*pilocarpinic acid, $C_{11}H_{14}O_4N_2Br_2$, is added to a concentrated warm aqueous solution of barium hydroxide, the solution soon becomes turbid, owing to the separation of barium oxalate; when the alkaline filtrate is distilled, ammonia and methylamine are formed, whilst barium carbonate separates. If, however, the excess of barium hydroxide is removed by carbon dioxide before the ammonia and methylamine are distilled off, and the solution then evaporated to a small bulk and alcohol added, barium pilomalate separates, whilst the solution contains methylcarbamide.

When dibromo*iso*pilocarpinic acid is heated with an excess of aqueous calcium hydroxide, solutions are obtained from which, on the addition of alcohol, calcium salts containing nitrogen are precipitated. The analyses of these salts point to the existence of an acid, $C_{11}H_{15}O_7N$.

When *iso*pilocarpine or its hydrochloride is heated with bromine and water, bromo*iso*pilocarpine perbromide, $C_{11}H_{15}O_2N_2Br,HBr_3$, is produced; it forms reddish-yellow prisms and melts at 123°. Bromo*iso*pilocarpine is formed by the action of sulphurous acid on it. This product is probably identical with Jowett's bromo*iso*pilocarpine.

*iso*Pilocarpoic acid has the probable constitution

$$CO_2H{\cdot}CHEt{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}C{<}\begin{matrix}NH{\cdot}CO\\ |\\ CH{\cdot}NMe\end{matrix}.$$

During the formation of pilocarpoic acid by the oxidation of pilocarpine with chromic acid, the lactone portion of the group $C_7H_{11}O_2$ in pilocarpine is oxidised thus:

$$\begin{matrix}CHEt{\cdot}CH{\cdot}CH_2{\cdot}\\ |\quad\quad |\\ CO{-}O{\cdot}CH_2\end{matrix} \longrightarrow \begin{matrix}CHEt{\cdot}CH{\cdot}CH_2{\cdot}\\ |\quad\quad |\\ CO{-}O{\cdot}CO\end{matrix}.$$

By the action of barium hydroxide, the latter group then yields the group $CO_2H\cdot CHEt\cdot CH(CO_2H)\cdot CH_2\cdot$.

The author considers that Jowett's formula for dibromo*iso*pilocarpinic acid (Trans., 1903, **83**, 441),

$$\begin{array}{l}\text{CHEt}\cdot\text{CH}\cdot\text{CH:CBr}\cdot\text{NMe}\cdot\text{CBr:N}\cdot\text{CO}_2\text{H}\\ \text{CO—O}\cdot\text{CH}_2\end{array},$$

is incorrect. He suggests the formula $\begin{array}{l}\text{CHEt}\cdot\text{CH}\cdot\text{CHBr}\cdot\text{CBr—NH}\\ \text{CO—O}\cdot\text{CH}_2\qquad\text{CO}\cdot\text{NMe}\end{array}\!\!>\!\text{CO}$, whilst for bromocarpic acid the formula

$$\begin{array}{l}\text{CHEt}\cdot\text{CH}\cdot\text{CHBr}\cdot\text{CO}\cdot\text{NMe}\cdot\text{CO}\cdot\text{NH}_2\\ \text{CO—O}\cdot\text{CH}_2\end{array}$$

is suggested. A. McK.

Thiopyrrolidone. JULIUS TAFEL and PAUL LAVACZECK (*Ber.*, 1905, **38**, 1592).—If a mixture of pyrrolidone and phosphorus trisulphide is heated at 150°, and, after evolution of hydrogen sulphide, cooled, powdered, and heated in a retort, at 350°, *thiopyrrolidone*, C_4H_7NS, distils as a yellow oil. On recrystallisation from a mixture of benzene and light petroleum, it forms colourless needles melting at 114°.

G. Y.

Action of Aniline on Anhydrocarboxylic Acids. W. BERTRAM (*Ber.*, 1905, **38**, 1615—1625).—In studying the action of aniline on anhydroaconitic acid, anhydroacetylcitronic acid, and other similar acids, the author has encountered a class of compounds which are both anilides and carboxylic acids. He proposes the name *anilidic acids* for these compounds, since the term anilic acids is used for the additive products of aniline and the anhydrides of dicarboxylic acids.

Aconite-monoanilidic acid, $CO_2H\cdot CH\!:\!C(CO_2H)\cdot CH_2\cdot CO\cdot NHPh$, obtained by the interaction of molecular proportions of aniline and anhydroaconitic acid in ethereal solution, crystallises from alcohol in yellow needles melting and decomposing at 141°, and dissolves readily in methyl alcohol or acetone. The *aniline* salt,

$$C_{12}H_{11}O_5N,C_6H_5\cdot NH_2,$$

prepared by the action of aniline (2 mols.) on anhydroaconitic acid (1 mol.), crystallises from methyl alcohol in silky leaflets which decompose and give up aniline even in the absence of light and air ; it melts at 107—108° and dissolves readily in alcohols and its acetone solution deposits the free acid. *Methyl aconitanilate*,

$$\text{NPh}<\!\begin{array}{l}\text{CO}\cdot\text{C:CH}\cdot\text{CO}_2\text{Me}\\ \text{CO}\cdot\text{CH}_2\end{array}\ (?),$$

crystallises in white leaflets or needles melting at 143 ; it dissolves slightly in water, giving a neutral solution, and more readily in alcohols ; on reduction with aluminium and acetic acid, this ester and also the ethyl and propyl esters yield the corresponding esters of tricarballylanilic acid, identical with those obtained by passing hydrogen chloride into the alcoholic solutions of aniline tricarballylanilate (*vide infra*). The *ethyl* ester, $C_{14}H_{13}O_4N$, crystallises in needles melting at 112°. The *propyl* ester, $C_{15}H_{15}O_4N$, is readily soluble in benzene and crystallises in needles

melting at 106°. The anilide, $C_{18}H_{14}O_3N_2$, prepared by the action of 3 mols. of aniline on 1 mol. of anhydroaconitic acid, has already been obtained by Pebal (*Annalen*, 1856, **98**, 79) and by Skinner and Ruhemann (Trans., 1889, **55**, 238).

Aconitic trimethylamide, $C_3H_3(CO\cdot NHMe)_3$, prepared by passing dry methylamine into an ice-cold solution of ethyl aconitate in an equal volume of ether, separates from ether in colourless, acicular crystals melting at 213—215°.

Aniline tricarballylmonoanilidate,

$$CO_2H\cdot CH_2\cdot CH(CO_2H)\cdot CH_2\cdot CO\cdot NHPh,C_6H_5\cdot NH_2 \text{ (?)},$$

prepared by the interaction of aniline (2 mols.) and anhydrotricarballylic acid, crystallises from alcohol in white needles melting at 127—128°, and is slightly soluble in benzene or water.

Methyl tricarballylanilate, $NPh<\begin{matrix}CO\cdot CH\cdot CH_2\cdot CO_2Me\\ CO\cdot CH_2\end{matrix}$, prepared by passing hydrogen chloride into an ice-cold saturated methyl-alcoholic solution of aniline tricarballylmonoanilidate, forms prismatic crystals melting at 106°, and is readily soluble in alcohols. The corresponding *ethyl* ester, $C_{14}H_{15}O_4N$, crystallises in slender, silky needles melting at 90°. The *propyl* ester, $C_{15}H_{17}O_4N$, crystallises in needles melting at about 55°. The *anilide of tricarballylanilic acid*, $C_{18}H_{16}O_3N_2$, crystallises in needles melting at 168° and has a neutral reaction.

The action of excess of aniline (more than 4 mols.) on anhydroacetylcitric acid (1 mol.) in ethereal solution yields: (1) *citrodianilidic acid*, $OH\cdot C(CH_2\cdot CO\cdot NHPh)_2\cdot CO_2H$, crystallises in slender leaflets melting and decomposing at 181°; on heating with 20 per cent. hydrochloric acid, it yields citric acid. When heated under about 12 mm. pressure, it gives carbon dioxide, water, aniline, citraconanil, a *substance* separating from alcohol in almost colourless plates, melting at 115°, and a *compound*, $C_{11}H_9O_2N$, which crystallises in metallic-looking, yellowish-green leaflets melting at 235—237°, and is moderately soluble in acetic acid or phenol.

(2) *Aniline citrodianilidate*, $C_{18}H_{18}O_5N_2,C_6H_5\cdot NH_2$, which separates in white needles melting at 152°.

(3) The *anilide of citroanilic acid*,

$$NPh<\begin{matrix}CO\cdot C(OH)\cdot CH_2\cdot CO\cdot NHPh\\ CO\cdot CH_2\end{matrix},$$

which crystallises in compact octahedra or long, silky needles melting at 182°.

Potassium citrodianilidate, $C_{18}H_{17}O_5N_2K$, crystallises in needles.

T. H. P.

Influence of Indifferent Solvents on the Alkylation of Organic Bases. ADOLF PINNER and A. FRANZ (*Ber.*, 1905, **38**, 1539—1548).—During the alkylation of organic bases, in addition to the rate of the reaction and the strength of the base, the solubility of the additive product in the solvent used is an important factor.

The base used was dissolved in an equal weight of solvent and the alkyl haloid added, the solution being kept cold. In certain cases, where the reaction was vigorous, an excess of solvent was taken. After

24—48 hours, the liquid was filtered and the amount of halogen in the crystalline residue was estimated. In such cases where the crystalline residue was suspected to contain quaternary salt, the residue was made alkaline with sodium hydroxide, extracted with ether, and the amount of halogen, both in the ether solution and in the liquid extracted, estimated.

By the action of methyl iodide (1 mol.) on piperidine (1 mol.) in ethereal solution, the salt of the secondary base, together with the quaternary ammonium salt, is formed; when methyl iodide (1 mol.) acts on piperidine (2 mols.), a mixture of the salt of the secondary base and the free tertiary base is formed.

When ethyl bromide (1 mol.) acts on piperidine (2 mols.), piperidine hydrobromide (1 mol.) and ethylpiperidine (1 mol.) are formed. The influence of the solvent was examined.

The behaviour of alkyl bromide was similar to that of ethyl bromide.

Amylpiperidine is best prepared, when ether is used as the solvent, from amyl bromide (1 mol.) and piperidine (2 mols.).

When ethyl chloroacetate acts on piperidine in ethereal solution at the ordinary temperature, the piperidine salt and ethyl piperidylacetate, $C_5NH_{10}\cdot CH_2\cdot CO_2Et$, are formed.

When benzyl chloride (1 mol.) acts on piperidine (1 mol.) in ethereal solution, piperidine hydrochloride is formed, whilst benzylpiperidine is present in the ethereal solution. When alcohol is used instead of ether as the solvent, a mixture of piperidine and benzylpiperidine salts is formed.

When ethyl bromide (1 mol.) acts on dipropylamine (1 mol.) at the ordinary temperature, dipropylamine hydrobromide is formed, whilst at 100° a mixture of the dipropylamine salt and the ethyldipropylamine salt is formed. This mixture is also produced when alcohol is used as a solvent and when the interaction takes place at the ordinary temperature; at 100°, the ethyldipropylamine salt only is formed.

By the interaction of molecular amounts of ethylamine and ethyl bromide, a mixture containing the salts of the primary and secondary bases, and possibly also of the tertiary base, is formed; in ethereal solution, the free tertiary base remains dissolved. The action of ethyl bromide on amylamine is similar.

When molecular quantities of benzylamine and ethyl bromide interact in ethereal solution, benzylamine salt separates, whilst benzylethylamine remains in the ethereal solution. A. McK.

Dinitrophenylpyridinium Chloride and its Transformation Products. III. Theodor Zincke (*Annalen*, 1905, **339**, 193—201).—It has been shown previously (Abstr., 1904, i, 448) that the dyes obtained from dinitrophenylpyridinium chloride and primary and secondary bases are the derivatives of an aldehyde alcohol or the corresponding imineamine, $OH\cdot CH{:}CH\cdot CH{:}CH\cdot CHO$ or

$$NH_2\cdot CH{:}CH\cdot CH{:}CH\cdot CH{:}NH.$$

By the decomposition of phenol in alkaline solution by chlorine, Hantzsch (Abstr., 1889, 853) obtained an acid, $C_6H_5O_4Cl_3$, which was finally converted into a compound, $C_5H_5O_2Cl$, thought to be a

cyclic diketone. Ince (Abstr., 1890, 1090) obtained coloured anilides and toluidides from this compound. It is now shown that this compound is the chloroaldehyde alcohol, OH·CH:CCl·CH:CH·CH·CHO, and that it yields coloured anilides analogous to those previously described.

It is unnecessary to isolate the compound $C_5H_5O_2Cl$, but the sodium salt, $C_6H_4O_4ClNa$, is directly treated with a solution of aniline in hydrochloric acid, when the dye begins to separate as *hydrochloride*, NHClPh:CH·CH:CH·CCl:CH·NHPh; it forms dark red leaflets, melting at 128—129°, and is converted into phenylchloropyridinium chloride by boiling with hydrochloric acid; the *chloride*, $C_5NH_4PhCl_2$, crystallises in needles; the *platinichloride*, $(C_{17}H_{16}N_2Cl)_2,PtCl_6$, crystallises in orange-red prisms or needles melting and decomposing at 195—196°. The *oxime*, NHPh·CH:CCl·CH:CH·CH:NOH, prepared from the dianilide, crystallises in yellow needles melting and decomposing at 152°. The *methylaniline* derivative,

NMePh·CH:CCl·CH:CH·CHO,

crystallises in yellow needles melting at 126—127°; it does not react with methylaniline, but with primary amines or phenylhydrazine; the *anilide*, NHPhCl:CH·CH:CH·CCl:CH·NMePh, crystallises in red needles melting and decomposing at 125—126°, the p-*chloroaniline* derivative, C_6H_4Cl·NHCl:CH·CH:CH·CCl:CH·NMePh, crystallises in red needles melting and decomposing at 130—132°. The *phenylhydrazone*, NHPh·N:CH·CH:CH·CCl:CH·NMePh, forms yellow needles or leaflets melting and decomposing at 147°.

The 2 : 4-*dinitroaniline* derivative,

$C_6H_3(NO_2)_2$·N:CH·CH:CH·CCl:CH·OH,

prepared from the sodium salt, forms dark red crystals melting and decomposing at 180°, and yields a phenylpyridinium chloride with hydrochloric acid. K. J. P. O.

Transformation of Indolinones into Alkylene Indolines. KARL BRUNNER (*Ber.*, 1905, **38**, 1359—1362. Compare Abstr., 1896, i, 625; 1897, i, 100, 438; 1898, i, 360, 384, 682; Decker and Hock, Abstr., 1904, i, 620).—2-*Benzylidene*-1 : 3 : 3-*trimethylindoline*,

$$C_6H_4<{CMe_2 \atop NMe}>C:CHPh,$$

prepared by decomposing with dilute acid the product of the action of magnesium benzyl chloride on 1 : 3 : 3-trimethylindoline-2-one in ethereal solution, crystallises from methyl alcohol in long, colourless needles, melts at 93°, and boils at 212° under 24 mm. pressure; the *hydriodide*, $C_{18}H_{20}NI$, crystallises from alcohol in yellow nodules melting and decomposing at 180°, the *platinichloride* forms orange-red leaflets and melts at 188° and the *stannichloride* melts at 186°. The base is rapidly oxidised by alkaline potassium permanganate; a warm alkaline solution of potassium ferricyanide converts it into 1 : 3 : 3-trimethylindoline-2-one, benzoic acid, and traces of benzaldehyde. W. A. D.

Preparation of Indophenols. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 157288).—The direct oxidation of a mixture of phenols and *p*-aminophenols to indophenols has not hitherto been

practicable. The oxidation takes place satisfactorily, however, at low temperatures. The solution of alkali phenoxide and *p*-aminophenol is added to a solution containing sodium hypochlorite, sodium chloride, and ice at a temperature of $-16°$ to $-17°$. The oxidation takes place rapidly, and the sodium derivative of the indophenol is precipitated in green, glistening crystals. The products dissolve in dilute alkali hydroxides to blue solutions, from which acids precipitate brownish-red powders, soluble in alcohol, ether, or chloroform.

C. H. D.

Ammonium Compounds. XIX. Nitration of Quaternary *cyclo*Ammonium Nitrates. HERMAN DECKER [with ST. GADOMSKA and M. GIRARD] (*Ber.*, 1905, **38**, 1274—1280. Compare this vol., i, 374).—*Quinoline methonitrate*, $C_9NH_7Me \cdot NO_3$, formed by adding the powdered methiodide to nitric acid of sp. gr. 1·4, is obtained on evaporation of the acid as a hygroscopic, white, crystalline mass, which melts at about 84°. When treated with nitric and sulphuric acids at the laboratory temperature, the methonitrate yields a mixture of 5- and 8-nitroquinoline methonitrates, which melts at about 190°. The isomerides cannot be separated as methonitrates, but after conversion into the methiodides and heating at 150°, 8-nitroquinoline is extracted by light petroleum, leaving 5-nitroquinoline methiodide.

8-*Nitroquinoline methonitrate*, $C_{10}H_9O_5N_3$, formed from 8-nitroquinoline methiodide or methosulphate, crystallises in yellow, hygroscopic needles and melts and decomposes at 160—170°.

5-*Nitroquinoline methonitrate* closely resembles the 8-nitro-compound, and melts and decomposes at 202—205°.

6-*Bromoquinoline methonitrate* forms white crystals, darkens at 220°, melts and decomposes at 228°, and on nitration and conversion into the methiodide yields 6-bromo-5-nitroquinoline methiodide.

3-*Bromoquinoline methonitrate* crystallises in white needles, becomes yellow at 160°, melts and decomposes at 207°, and on nitration yields 3-*bromo*-5-*nitroquinoline methonitrate*, which crystallises in yellow scales, melts and decomposes at 159°, and is not hygroscopic.

8-*Methylquinoline methonitrate*, $C_{11}H_{12}O_3N_2$, forms white crystals, melts at about 72°, is very easily soluble in water, and on nitration and oxidation of the product with alkaline potassium ferricyanide yields 5-nitro-1 : 8-dimethylquinoline.

6-*Methylquinoline methonitrate* crystallises in white, hygroscopic needles, and on nitration and treatment with methyl iodide yields 5-nitro-6-methylquinoline methiodide.

When nitrated at 35—40°, the additive compound of papaverine and methyl sulphate yields nitropapaverine methonitrate, which, when boiled in dilute alkaline solution, forms nitrobromoveratrole and dimethoxymethyl*iso*quinolone.

G. Y.

Replacement of Bromine by Chlorine in Quinoline Derivatives and Halogenated 8-Hydroxyquinolones. JOH. HOWITZ and KURT WITTE (*Ber.*, 1905, **38**, 1260—1270. Compare Abstr., 1903, i, 279; this vol., i, 375).—5-*Chloro*-6-*ethoxyquinoline*,

$$C_9NH_5Cl \cdot OEt, H_2O,$$

formed by boiling 5-chloro-6-hydroxyquinoline with sodium hydroxide and ethyl bromide in alcoholic solution in a reflux apparatus, crystallises in yellow needles, which weather on exposure to the air, and melts at 75°. The *methiodide*, $C_{12}H_{13}ONClI,H_2O$, forms red prisms and melts and decomposes at 187°; the *ethiodide* forms slender, yellow needles or thick, red crystals and melts at 206°. 5-*Chloro*-6-*ethoxy*-1-*methylquinolone*, $C_9NH_4OClMe{\cdot}OEt$, is formed by the oxidation of the methiodide with potassium ferricyanide in cooled alkaline solution; it crystallises in yellow needles, melts at 136°, and, when heated with concentrated hydrochloric acid at 160—170°, yields 5-chloro-6-hydroxy-1-methylquinolone (Abstr., 1903, i, 279). 5-*Chloro*-6-*ethoxy*-1-*ethylquinolone*, formed by oxidation of the ethiodide with potassium ferricyanide, crystallises in clear plates containing $3H_2O$, melts at 72°, or, when anhydrous, at 102°, and when heated with concentrated hydrochloric acid at 160—170° yields 5-chloro-6-hydroxy-1-ethylquinolone (*loc. cit.*).

7-*Bromo*-8-*methoxyquinoline*, formed by boiling 7-bromo-8-hydroxyquinoline with sodium hydroxide and methyl iodide in methyl-alcoholic solution, crystallises in slender needles and melts at 78°. The *methiodide* crystallises in brown needles and melts and decomposes at 154°. 7-*Bromo*-8-*methoxy*-1-*methylquinolone*, formed by oxidation of the methiodide with alkaline potassium ferricyanide, crystallises in small prisms and melts at 75°, and when boiled with hydrobromic acid yields 7-*bromo*-8-*hydroxy*-1-*methylquinolone*, which crystallises in small, colourless needles, melts at 176°, and forms a sparingly soluble *sodium* derivative. Hydrolysis of the bromomethoxymethylquinolone with concentrated hydrochloric acid at 160° leads to the formation of 7-*chloro*-8-*hydroxy*-1-*methylquinolone*, $C_{10}H_8O_2NCl,H_2O$, which crystallises in colourless needles, loses H_2O at 110°, and melts at 247°.

5-*Bromo*-8-*methoxyquinoline*, $C_{10}H_8ONBr,3H_2O$, formed by boiling the hydroxyquinoline with sodium hydroxide, methyl iodide, and methyl alcohol, crystallises in slender, colourless needles, which weather on exposure to the air; it melts at 82°. The *methiodide* forms flat, brown crystals and melts at 161°. 5-*Bromo*-8-*methoxy*-1-*methylquinolone*, obtained by oxidation of the methiodide, crystallises in slender, felted needles, melts at 145°, and when boiled with concentrated hydrobromic acid, yields 5-*bromo*-8-*hydroxy*-1-*methylquinolone*, which crystallises in small, colourless needles, melts at 207°, and forms a sparingly soluble *sodium* salt. Hydrolysis of the bromomethoxy-compound with concentrated hydrochloric acid at 170° leads to the formation of 5-*chloro*-8-*hydroxy*-1-*methylquinolone*, which crystallises in colourless needles and melts at 251°.

5 : 7-*Dibromo*-8-*methoxyquinoline*, $C_{10}H_7ONBr_2$, crystallises in slender needles, which slowly become violet, and melts at 99°. The *methiodide* crystallises in brown needles, melts at 174°, and on oxidation is converted into 5 : 7-*dibromo*-8-*methoxy*-1-*methylquinolone*, which forms slender, yellow needles and melts at 166°. 5 : 7-*Dibromo*-8-*hydroxy*-1-*methylquinolone* crystallises from glacial acetic acid in transparent, yellow needles, which contain acetic acid, and on exposure to the air rapidly weather to a powder, melting at 209°. 5 : 7-*Dichloro*-8-

hydroxy-1-*methylquinolone*, obtained by heating dibromomethoxymethylquinolone with concentrated hydrochloric acid at 160—170°, crystallises in glistening needles and melts at 258°.

5-Bromo-6-hydroxy-, 5-bromo-8-hydroxy-, 7-bromo-8-hydroxy-, and 5 : 7-dibromo-8-hydroxy-quinolines yield the corresponding bromohydroxyquinolines when heated with concentrated hydrochloric acid at 160—170°. G. Y.

Derivatives of 8-Quinolinealdehyde. Joh. Howitz and Wilhelm Schwenk (*Ber.*, 1905, 38, 1280—1289. Compare Abstr., 1902, i, 397).—The *hydrochloride* of 8-quinolinealdehyde,

$$C_{10}H_7ON,HCl,$$

forms white crystals and melts at 213°; the *hydriodide* forms nodular aggregates of red crystals and melts and decomposes at 228°. The *oxime*, $C_9NH_6\cdot CH{:}NOH,\frac{1}{2}H_2O$, crystallises in small, glistening leaflets and melts at 115°. The *anil*, $C_9NH_6\cdot CH{:}NPh$, forms yellow crystals and melts at 82°; the o-*tolil*, $C_{10}H_7N{:}N\cdot C_7H_7$, crystallises in yellow needles and melts at 105°. The *azine*, $C_9NH_6\cdot CH{:}N\cdot N{:}CH\cdot C_9NH_6$, crystallises in slender, yellow needles and melts at 248—249°; the *phenylhydrazone*, $C_9NH_6\cdot CH{:}N\cdot NHPh$, crystallises in yellow needles and melts at 176°; the *semicarbazone*, $C_{11}H_{10}ON_4$, crystallises in slender, white needles and melts at 238—239° When heated with dimethylaniline and zinc chloride, 8-quinolinealdehyde forms tetramethyldiaminodiphenyl-8-quinolylmethane, $C_9NH_6\cdot CH(C_6H_4\cdot NMe_2)_2$, which crystallises in colourless needles, melts at 179—180°, and when oxidised by lead peroxide yields an intense green *dye*; this forms a green, crystalline *zincochloride*.

3-*Bromo*-8-*bromomethylquinoline*, $C_9NH_5Br\cdot CH_2Br$, is formed in small amount in the preparation of 8-bromomethylquinoline, or in large amount by heating the dibromide of 8-methylquinoline hydrobromide at 180° until the evolution of hydrogen bromide ceases, and then adding 1 mol. of bromine. It crystallises in glistening, silvery leaflets, melts at 106°, and is a weak base; the *platinichloride* forms a yellow, crystalline precipitate. When boiled with alcoholic potassium hydroxide in a reflux apparatus, the dibromo-compound forms 3-*bromo*-8-*hydroxymethylquinoline*, $C_9NH_5Br\cdot CH_2\cdot OH$, which crystallises in white needles, melts at 51°, and is oxidised by potassium permanganate in alkaline solution to 5-bromopyridine-2 : 3-dicarboxylic acid. The *phenyl ether* of 3-bromo-8-hydroxymethylquinoline,

$$C_9NH_5Br\cdot CH_2\cdot OPh,$$

is formed by boiling 3-bromo-8-bromomethylquinoline with potassium phenoxide in alcoholic solution; it crystallises in long, white needles and melts at 102—103°.

3-*Bromo*-8-*quinolinealdehyde*, $C_9NH_5Br\cdot CHO$, formed by the oxidation of the corresponding alcohol with nitric acid of sp. gr. 1·4, crystallises in white needles and melts at 168°. The *oxime*,

$$C_{10}H_7ON_2Br,$$

crystallises in slender, white needles and melts at 188°; the *azine*, $C_{20}H_{12}N_4Br_2$, crystallises in yellow needles and melts at 268°; the *anil*, $C_{16}H_{11}N_2Br$, forms long, yellow needles and melts at 142°; the

semicarbazone, $C_{11}H_9ON_4Br$, crystallises in white needles and melts at 250°.

3-*Bromoquinoline*-8-*carboxylic acid*, $C_9NH_5Br{\cdot}CO_2H$, formed by oxidation of the aldehyde with chromic acid in sulphuric acid solution, crystallises in glistening, slender, white needles, melts at 206—207°, and sublimes without decomposition. The *barium* salt,

$$(C_{10}H_5O_2NBr)_2Ba,$$

crystallises in glistening, slender, white needles.

8-Bromomethylquinoline cannot be oxidised directly to 8-quinolinealdehyde, but is converted by alcoholic potassium hydroxide into 8-hydroxymethylquinoline, which is oxidised to the aldehyde by nitric acid. G. Y.

Introduction of the Benzoyl Group into Tertiary Cyclic Bases. Arnold Reissert (*Ber.*, 1905, **38**, 1603—1614).—Although pyridine reacts very energetically with acid chlorides, forming additive compounds, quinoline exhibits no analogous reaction. In presence of sodium hydroxide or potassium cyanide, however, quinoline and benzoyl chloride react, giving the following products.

2-*Hydroxy*-1-*benzoyl*-1 : 2-*dihydroquinoline*,

$$\begin{array}{l} CH{\cdot}CH{:}C{\cdot}CH{=}CH \\ CH{\cdot}CH{:}C{\cdot}NBz{\cdot}CH(OH) \end{array},$$

prepared by the action of excess of benzoyl chloride on quinoline in presence of sodium hydroxide, crystallises from alcohol in shining, colourless needles melting at 182°, and dissolves readily in acetic acid. By acetic acid or dilute mineral acids, it is converted into benzoic acid and quinoline, whilst concentrated sulphuric acid transforms it into reddish-yellow, resinous products. It is dissolved and gradually decomposed by alcoholic sodium hydroxide solution. On oxidation with potassium permanganate in the cold, it yields benzoylanthranilic acid, isatinic acid, and a small proportion of a *compound* which crystallises from aqueous alcohol in slender needles melting at 73°.

2-*Cyano*-1-*benzoyl*-1 : 2-*dihydroquinoline*, $\begin{array}{l} CH{\cdot}CH{:}C{\cdot}CH{=}CH \\ CH{\cdot}CH{:}C{\cdot}NBz{\cdot}CH{\cdot}CN \end{array}$,

obtained by the action of benzoyl chloride on quinoline in presence of potassium cyanide, crystallises from alcohol in hard, shining prisms melting at 154—155°, and is readily soluble in benzene, chloroform, acetone, or acetic acid. By means of concentrated mineral acids, it is resolved into benzaldehyde, quinaldinic acid and its amide, and the *benzoin ester* of *quinoline*-2-*carboxylic acid*, $C_9H_6N{\cdot}CO{\cdot}O{\cdot}CHPhBz$, which crystallises from alcohol in microscopic, pointed prisms melting at 168—168·5° and is readily soluble in benzene, acetic acid, ethyl acetate, chloroform, or acetone, and slightly so in methyl or ethyl alcohol. T. H. P.

Papaverinium Bases. III. Herman Decker and Otto Koch (*Ber.*, 1905, **38**, 1739—1741. Compare Abstr., 1904, i, 338, 926).—*Dimethoxy*iso*quinoline methiodide*, $C_{12}H_{14}O_2NI,H_2O$, prepared by the action of methyl iodide or of methyl sulphate on dimethoxy*iso*quinoline, melts at 236—237°. The *picrate* melts at 209° and is explosive.

Dimethoxy-2-methyl*iso*quinolone, prepared by the action of an excess of potassium ferricyanide on the methiodide, separates as a flocculent mass, which yields the hydrochloride melting at 185—186°.

Dimethoxy-2-benzyl*iso*quinolone, prepared from benzyl chloride and dimethoxy*iso*quinoline in an analogous manner, melts at 165° and is identical with the product previously prepared from benzyl*iso*-papaverine (*loc. cit.*).

Piperonyl alcohol is best prepared by Cannizaro's method. When a current of benzene is passed into a solution of piperonyl alcohol in benzene at 0°, *piperonyl chloride* is formed; it crystallises in white needles, melts at 23°, and does not form a magnesium compound when its ethereal or anisole solution is heated with magnesium. A. McK.

Stereoisomeric Conhydrinium Iodides. Max Scholtz and P. Pawlicki (*Ber.*, 1905, 38, 1289—1295. Compare Abstr., 1904, i, 1044; this vol., i, 296).—Conhydrine has $[\alpha]_D + 10°$. 1-Ethylconhydrine boils at 227—228° (corr.) and has a sp. gr. 0·9345 at 20°/4°, $[\alpha]_D - 45·2°$, and $[M]_D - 77°$.

By the action of benzyl iodide on 1-ethylconhydrine, a mixture of two stereoisomeric benzylethylconhydrinium iodides is formed; these can be separated by fractional precipitation by ether from the chloroform solution. The *α-iodide*, $C_{17}H_{28}ONI$, which is the more soluble in the mixture of chloroform and ether, melts at 163°; the *β-iodide* melts at 188°. These two iodides yield the same derivatives; the *platinichloride* crystallises from water and melts at 191°; the *mercurichloride* and *picrate* are oils. By the action of ethyl iodide on 1-ethylconhydrine, only Wertheim's diethylconhydrinium iodide (*Jahresber.*, 1863, 435) is formed.

1-Propylconhydrine boils at 240—241° (corr.) and has a sp. gr. 0·9172 at 20°/4°, $[\alpha]_D - 50·1°$, and $[M]_D - 93°$. With benzyl iodide, it forms a mixture of two stereoisomeric benzylpropylconhydrinium iodides, which are separated by recrystallisation from water. The *α-iodide*, $C_{18}H_{30}ONI,2H_2O$, crystallises in glistening, short prisms on slow evaporation of its aqueous solution, melts at 55°, loses $2H_2O$ at 100°, and, when anhydrous, melts and changes into the β-isomeride at 161°. The *β-iodide* crystallises from water in colourless needles and melts at 180°. Both iodides give the same crystalline *platinichloride*, which melts at 201—202°.

1-iso*Amylconhydrine* is a colourless oil, which boils at 272—273° (corr.) and has a sp. gr. 0·9087, $[\alpha]_D - 45·1°$, and $[M]_D - 96°$. A mixture of two stereoisomeric benzyl*iso*amylconhydrinium iodides, which can be separated by recrystallisation from water, is formed by the action of benzyl iodide on *N-iso*amylconhydrine. The *α-iodide*, $C_{20}H_{34}ONI$, which is the more soluble in water, melts at 165° and has $[\alpha]_D - 40°$ at 20°; the *β-iodide* melts at 185° and has $[\alpha]_D - 50°$ at 20°. Both iodides yield the same *platinichloride*, $(C_{20}H_{34}ON)_2PtCl_6$, which melts at 195°, and *mercurichloride*, which melts at 197°.

1-*Ethyl-2-methyltetrahydroquinoline*, formed by the action of ethyl iodide and potassium hydroxide on dextrorotatory 2-methyltetrahydroquinoline (Ladenberg, Abstr., 1894, i, 208), boils at 256° (corr.), has

a sp. gr. 0·9942 at 20°/4° and $[\alpha]_D$ +12·1° at 20°, and, when warmed with benzyl iodide, forms only one 1-*benzyl*-1-*ethyl*-2-*methyltetrahydroquinolinium iodide*, $C_{19}H_{24}NI$, which crystallises in orange-red leaflets and melts at 161°. G. Y.

Benzidine Salts (Hydrofluoride and Hydrosilicofluoride). Richard Ehrenfeld (*Chem. Zeit.*, 1905, **29**, 422—424).—When benzidine is heated with an excess of hydrofluoric acid, a mixture of the salts $C_{12}H_8(NH_2)_2$,5HF and $C_{12}H_8(NH_2)_2$,6HF is formed. At the ordinary temperature, benzidine interacts with hydrofluoric acid to form the salt $C_{12}H_8(NH_2)_2$,2HF, and sometimes, under certain conditions, it yields the salt $C_{12}H_8(NH_2)_2$,3HF.

Solutions of benzidine hydrochloride were added to solutions of ammonium fluoride and sodium fluoride respectively, which were heated to boiling in platinum vessels. The number of molecules of hydrogen fluoride with which benzidine combines under these conditions depends on the amount of free hydrochloric acid in the solution of benzidine hydrochloride added. Benzidine may unite with from 1 to 6 mols. of hydrogen fluoride.

The *salt* $C_{12}H_8(NH_2)_2,H_2SiF_6$, prepared by the action of boiling hydrofluosilicic acid on a solution of benzidine hydrochloride, forms silvery, hexagonal crystals. A. McK.

Constitution of Diketobutyric Ester Phenylhydrazones. André Wahl (*Bull. Soc. chim.*, 1905, [iii], **33**, 490—495. Compare Abstr., 1904, i, 556, 789, and this vol., i, 408).—Most of the results recorded in this paper have already been published (Abstr., 1904, i, 789). The product of the action of *p*-nitrophenylhydrazine on ethyl diketobutyrate β-phenylhydrazone is now regarded as 1-phenyl-3-methyl-5-pyrazolone-4-*p*-nitrophenylhydrazone (compare Bülow, Abstr., 1899, i, 271). By the action of phenylhydrazine on ethyl diketobutyrate, dissolved in boiling alcohol or in ether, in presence of zinc chloride, 1-phenyl-3-methyl-5-pyrazolone-4-phenylhydrazone is formed (compare Abstr., 1904, i, 789). The author considers that this synthesis affords a new proof of the hydrazinic constitution of this compound advocated by Sachs and Barschall (Abstr., 1902, i, 503) as against the azoic constitution proposed by Bülow (Abstr., 1899, i, 356, and Eibner, 1903, i, 871). T. A. H.

Hydrazones derived from *o*-, *m*-, and *p*-Nitrophenylhydrazines. William Alberda van Ekenstein and Jan J. Blanksma (*Rec. trav. chim.*, 1905, **24**, 33—39. Compare Abstr., 1904, i, 98).—Methods are described for the estimation of acetone, diethyl ketone, acetaldehyde, and benzaldehyde, and for the separation of dextrose, lævulose, or mannose from sucrose, by the conversion of these aldehydes or ketones into their respective *p*-nitrophenylhydrazones. It is probable that the same method may also be applied to the separation of the hexoses from maltose and lactose, since the *p*-nitrophenylhydrazones of the latter are readily soluble.

Glycuronic acid p-*nitrophenylhydrazone* forms yellow crystals, melts at 225°, has $[\alpha]_D$ −91·2° (in pyridine and ethyl alcohol), and dissolves in warm water, sparingly in alcohol, ether, and chloroform. This

derivative may be used for the detection of small quantities of the acid. *Lyxose* p-*nitrophenylhydrazone* separates from alcohol in yellow crystals, melts at 172°, and has $[\alpha]_D + 32{\cdot}2°$.

The m-*nitrophenylhydrazones* of the following aldehydes and ketones were prepared by warming them, dissolved in alcohol, for a few minutes with *m*-nitrophenylhydrazine: diethyl ketone (m. p. 105°), *o*-, *m*-, and *p*-nitrobenzaldehydes (m. p. 205°, 213°, and 228° respectively), benzophenone (m. p. 138°), acetophenone (m. p. 163°), salicylaldehyde (m. p. 197°), *p*-tolualdehyde, (m. p. 155°), cinnamaldehyde (m. p. 146°), and furfuraldehyde (m. p. 137°).

Dextrose m-*nitrophenylhydrazone* melts at 110° and has $\alpha_D - 6{\cdot}3°$; the corresponding *derivative* of mannose melts at 162° and has $\alpha_D + 10{\cdot}7°$, that of galactose melts at 182° and is optically inactive, that of rhamnose melts at 156° and has $\alpha_D - 21{\cdot}4°$, and the *arabinose* compound melts at 182° and is optically inactive. These derivatives of the hexoses crystallise readily, are yellow, soluble in boiling alcohol, sparingly soluble in water, and the respective sugars are regenerated on treatment with benzaldehyde.

The o-*nitrophenylhydrazones* of the following substances were prepared: acetone (m. p. 70°), diethyl ketone (m. p. 60°), formaldehyde (m. p. 85°), acetaldehyde (m. p. 124°), *o*-, *m*-, and *p*-nitrobenzaldehydes (m. p. 225°, 230°, and 255° respectively), *o*- and *p*-hydroxybenzaldehydes (m. p. 193° and 235° respectively), *p*-tolualdehyde (m. p. 183°), acetophenone (m. p. 138°), benzophenone (m. p. 161°), furfuraldehyde (m. p. 155°), and cinnamaldehyde (m. p. 190°).

The o-*nitrophenylhydrazone* of dextrose melts at 158° and has $\alpha_D + 27{\cdot}8°$, and the corresponding *derivatives* of lævulose (m. p. 162°, $\alpha_D + 31°$), mannose (m. p. 171°, $\alpha_D + 16°$), galactose (m. p. 178°, $\alpha_D - 26{\cdot}8°$), rhamnose (m. p. 162°, $\alpha_D - 59°$), and arabinose (m. p. 172°, $\alpha_D - 21{\cdot}4°$) were prepared. Lævulose-*o*-nitrophenylhydrazone, which crystallises in bright red needles, is less soluble in alcohol than the dextrose derivative, and it is possible to separate these two sugars by this means. Galactose-*o*-nitrophenylhydrazone is gelatinous and in this respect resembles the benzylallyl- and phenylamyl-hydrazones of this sugar. T. A. H.

Antipyrylsemicarbazide. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and H. BARBIER (*Bull. Soc. chim.*, 1905, [iii], **33**, 503—505).—*Antipyrylsemicarbazide*, $\begin{matrix}NMe{\cdot}CMe \\ | \\ NPh{-}CO\end{matrix}\!\!>\!C{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH_2$, prepared by the action of hydrazine on antipyrylcarbamide, is a crystalline powder, melts at 135°, and is readily soluble in water or alcohol, less so in ether or benzene. The *salts* are difficult to crystallise. The *acetyl* derivative crystallises from boiling alcohol in colourless needles and melts at 214—215°. *β-Propylideneantipyrylsemicarbazide*, obtained by condensing acetone with antipyrylsemicarbazide, forms colourless crystals and melts at 209—210°. *Benzylideneantipyrylsemicarbazide* occurs in colourless needles and melts at 225°, and the corresponding *product* prepared from ethyl acetoacetate crystallises from alcohol in needles and melts at 207°. With phenylcarbimide, antipyrylsemicarbazide yields the corresponding *phenylcarbamide*, which is crystalline and melts

at 236°, and with ethyl chlorocarbonate the corresponding *urethane*, which occurs in colourless needles and melts at 207°. T. A. H.

Glyoxalines. ADOLF PINNER (*Ber.*, 1905, **38**, 1531—1538).—By the action of ammonia on phenylglyoxal, a mixture of the isomerides 2-benzoyl-5-phenylglyoxaline and 3-hydroxy-1 : 4-diphenylpyrazine melting at 202° is produced (compare Abstr., 1903, i, 123). By the action of methyl iodide on the former compound, a methiodide is formed from which, by the action of potassium hydroxide, methylamine is eliminated, whilst the latter compound forms a methyl ether.

2-Benzoyl-5-phenylglyoxaline, $\begin{matrix}\mathrm{NH{-}CBz}\\ \mathrm{CPh{:}CH}\end{matrix}\!\!>\!\mathrm{N}$, separates from pyridine in yellow prisms and melts at 280°. It reacts with methyl iodide and potassium hydroxide at 100° to form *2-benzoyl-5-phenyl-1-methylglyoxaline methiodide*, which melts and decomposes at 216°.

Phenylglyoxaline, $\begin{matrix}\mathrm{NH{-}CH}\\ \mathrm{CPh{:}CH}\end{matrix}\!\!>\!\mathrm{N}$, when heated for 8 hours at 100° with a mixture of ethyl bromide and alcohol, forms *5-phenyl-1-ethylglyoxaline*, $\begin{matrix}\mathrm{NEt{-}CH}\\ \mathrm{CPh{:}CH}\end{matrix}\!\!>\!\mathrm{N}$, the *platinichloride* of which melts and decomposes at 197°. When boiled with an aqueous solution of sodium hydroxide, phenylethylglyoxaline yields ethylamine.

Diphenylglyoxaline is best prepared by the action of ammonia on a mixture of formaldehyde and benzil at a low temperature. *4 : 5-Diphenyl-1-ethylglyoxaline*, $\begin{matrix}\mathrm{NEt{-}CH}\\ \mathrm{CPh{:}CPh}\end{matrix}\!\!>\!\mathrm{N}$, prepared by the alkylation of diphenylglyoxaline by ethyl bromide, forms rhombic prisms and melts at 94—95°; its *hydrochloride* forms rhombic prisms and decomposes at 260°; its *platinichloride* melts and decomposes at 225°, whilst its *hydrobromide* forms glistening, rhombic crystals, which melt and decompose at 260°.

4 : 5-Diphenyl-1 : 3-diethylglyoxalinium bromide, $\begin{matrix}\mathrm{NEt{-}CH}\\ \mathrm{CPh{:}CPh}\end{matrix}\!\!>\!\mathrm{NEtBr}$, crystallises in glistening prisms and melts at 153—154°. When boiled with an aqueous solution of potassium hydroxide, ethylamine and a carbylamine are formed. A. McK.

5-Aminopyrazole and Iminopyrine. AUGUST MICHAELIS (*Annalen*, 1905, **339**, 117—193).—The pyrines are derivatives of the pyrazoles, in which an alkyl group is attached to the nitrogen atom in position 2, and have a bivalent group or atom, oxygen, sulphur, selenium, or the imino-group, attached at the same time to position 2 and either position 3 or 5; the nitrogen atom in position 2 is therefore quinquevalent, thus : $\begin{matrix}\mathrm{-C{:}NAlk.}\\ \mathrm{NPh}\\ \mathrm{-C{:}C}\end{matrix}\!\!>\!\mathrm{NH}$ (or O, S, or Se) or

$$\mathrm{-C}\!\!<\!\!\begin{matrix}\mathrm{NPh\cdot NAlk.}\\ \mathrm{C{-}{-}C}\end{matrix}\!\!>\!\mathrm{NH}\ \text{(or O, S, or Se).}$$

Knorr, on the other hand, thinks that there is only one ring, the bivalent atom or group being linked exclusively to position 3 or 5.

The name "iminopyrine" is given to the 1-phenyl-2 : 3-dimethyl-iminopyrazole, which corresponds with antipyrine. The iminopyrines are prepared either by the action of alkali hydroxides on the methiodide of 5-aminopyrazoles or from antipyrine chlorides (5-chloropyrazole-methiodide) by the action of ammonia or a primary amine. They are strong bases, either liquid or solid, which absorb carbon dioxide from the air. They form additive compounds with alkyl iodides, the second ring being broken, thus: $\begin{matrix}-C = N(AlkI) \\ \vert \\ -C{:}C(NMePh)\end{matrix}\!\!>\!NPh$. Similarly, acid chlorides combine with the iminopyrines, forming compounds which are strong bases. The conductivity and other properties of the solutions point to their containing an ammonium hydroxide formed from the iminopyrine by addition of water, the second ring being broken, thus: $\begin{matrix}-C{:}NMe(OH) \\ \vert \\ -C : C(NHX)\end{matrix}\!\!>\!NPh$. On addition of alkali, the anhydride, that is, the iminopyrine, is again formed.

[With Eduard Brust.]—5-*Amino*-1-*phenyl*-3-*methylpyrazole*,

$$CH\!\!<\!\!\begin{matrix}CMe{:}N \\ C(NH_2)\end{matrix}\!\!>\!NPh,$$

prepared by heating under pressure a mixture of antipyrine chloride and ammonium carbonate at 300°, crystallises in needles melting at 116° and boiling at 333°; it reduces silver, but not Fehling's solution; it gives an intense red precipitate with potassium bismuth iodide, and a blue coloration with a mixture of ferric chloride and potassium ferricyanide. Bleaching powder in the presence of acetic acid converts it into a red compound containing chlorine, whilst nitrous acid leads to the formation of a compound $C_{10}H_8ON_4$; the *hydrochloride*, $C_{10}H_{11}N_3,HCl$, is a powder melting at 198°. The *mercurichloride*, $C_{10}H_{11}N_3,HgCl_2$, is a white precipitate decomposed on heating. The *platinichloride*, $(C_{10}H_{11}N_3)_2,H_2PtCl_6$, crystallises in reddish-yellow needles melting at 169°; the *aurichloride* is a reddish-brown precipitate melting at 90°. The *ferrocyanide*,

$$(C_{10}H_{11}N_3)_2,H_4Fe(CN)_6,$$

crystallises in leaflets, and the *picrate*, $C_{10}H_{11}N_3{\cdot}C_6H_3O_7N_3$, in yellow scales melting at 160—162°. 5-*Acetylamino*-1-*phenyl*-3-*methylpyrazole* is a crystalline solid melting at 110°, and does not give a coloration with bleaching powder; its *chloro*-derivative, $CCl\!\!<\!\!\begin{matrix}CMe = N \\ C(NHAc)\end{matrix}\!\!>\!NPh$, prepared by leading chlorine into its acetic acid solution, crystallises in needles melting at 132—133°. On hydrolysis, it yields 4-*chloro*-5-*amino*-1-*phenyl*-3-*methylpyrazole*, which can also be obtained directly from the 5-amino-compound; it crystallises in yellow needles melting at 118°. Prolonged chlorination of the aminopyrazole results in the formation of the *hydrochloride* of 4-*chloro*-5-*amino*-1-*dichlorophenyl*-3-*methylpyrazole*, $CCl\!\!<\!\!\begin{matrix}CMe{:}N \\ C(NH_2)\end{matrix}\!\!>\!N{\cdot}C_6H_3Cl_2$, which is decomposed by water, the base being a yellow solid decomposing on heating. 4-*Bromo*-5-*amino*-1-*phenyl*-3-*methylpyrazole*, $C_{10}H_{10}N_3Br$, prepared by brominating aminopyrazole, crystallises in scales melting at 106·5°; the corresponding *iodo*-compound crystallises in leaflets melting at 75°, and gives a white precipitate with mercuric chloride. 4-*Benzeneazo*-5-

amino-1-phenyl-3-methylpyrazole, prepared from the aminopyrazole and diazobenzene, crystallises in dark yellow leaflets melting at 140°; its *hydrochloride* is dark red and melts at 170°. 5-*Amino-1-nitrophenyl-3-methylpyrazole,* $CH\lessdot\begin{matrix}CMe:N\\C(NH_2)\end{matrix}\gt N\cdot C_6H_4\cdot NO_2$, prepared by nitrating the aminopyrazole, is a yellow solid melting at 98—99°.

5-*Ethylamino-1-phenyl-3-methylpyrazole,* prepared by heating antipyrine chloride and anhydrous ethylamine at 150°, is a liquid boiling at 315° and gives, with mercuric chloride, a white double salt. The corresponding *dimethylamine* derivative is a yellow oil boiling at 297°, and the *diethylamine* derivative a yellow oil boiling at 306—307°; the *platinichloride* of the latter, $(C_{14}H_{19}N_3)_2,H_2PtCl_6$, crystallises in reddish-yellow leaflets melting at 168°.

5-*Amino-1-phenyl-3:4-dimethylpyrazole,* prepared by heating the methiodide of chlorophenyldimethylpyrazole with ammonium carbonate at 250°, forms white crystals melting at 102° and boiling at 336°; the *hydrochloride* forms white crystals melting at 70°, and the *picrate* yellow crystals melting at 137—138°. It also yields a *nitro*-derivative melting at 87°.

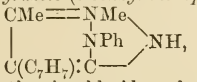
The *methiodide* of 5-*amino-1-phenyl-3-methylpyrazole* (*iminopyrine hydriodide*), $\begin{matrix}CMe:N(MeI)\\ | \\ CH:C(NH_2)\end{matrix}\gt NPh$, prepared by heating 5-aminopyrazole with methyl iodide at 100°, forms crystals melting at 182°; it also crystallises with $\frac{1}{2}H_2O$, and then sinters at 83° and melts at 163°. The *platinichloride,* $(C_{11}H_{14}N_3)_2,H_2PtCl_6$, melts at 207°. The free *iminopyrine* can be prepared from the iodide or, better, from the chloride by treatment with sodium hydroxide. The corresponding *ethyliminopyrine hydriodide* crystallises in needles melting at 206—207°. 2:5-*Imino-1-phenyl-3-methyl-2-ethylpyrazole* (2-*ethyliminopyrine*), $C\begin{matrix}\diagup CH\cdot CMe \diagdown \\ -NPh- \\ \diagdown NH \diagup\end{matrix}NEt$, prepared from the compound last mentioned or by treatment of the ethiodide of 5-iodo-1-phenyl-3-methylpyrazole with ammonia at 180°, is a thick yellow oil. The *platinichloride* crystallises in red needles melting at 192—195°; the *picrate* forms yellow prisms melting at 172°, and the *benzenesulphonic* derivative colourless crystals melting at 173°.

[With WILHELM PREUNER.]—5-*Amino-1-phenyl-4-benzyl-3-methylpyrazole,* $C_7H_7\cdot C\lessdot\begin{matrix}CMe:N\\C(NH_2)\end{matrix}\gt NPh$, prepared by heating the methiodide of 5-chloro-4-benzylpyrazole with ammonium carbonate under pressure at 210°, forms colourless crystals melting at 77°; the *hydrochloride* crystallises in microscopic needles melting at 187°, and the *picrate* in yellow needles melting at 140°; the *benzoyl* derivative crystallises in prisms melting at 184°.

1-*Phenyl-4-benzyl-3-methylpyrazolone* appears to exist in two modifications; if in the preparation of 5-chloro-1-phenyl-4-benzyl-3-methylpyrazole from it a small quantity of phosphorus oyxchloride is used, colourless crystals of a modification of the pyrazolone are obtained melting at 147·5°, which pass slowly into the ordinary form melting at 136°.

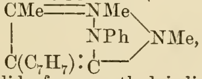
5-*Methylamino-1-phenyl-4-benzyl-3-methylpyrazole* (ψ-4-*benzylamino-*

pyrine), $C_7H_7\cdot C\Big\langle{}^{CMe=N}_{C(NHMe)}\Big\rangle NPh$, is formed on distilling 4-benzyliminopyrine under reduced pressure, and crystallises in prisms melting at 120·5° and boiling at 236° under 17 mm. pressure. 2 : 5-*Imino*-1-*phenyl*-4-*benzyl*-3-*methylpyrazole* (4-*benzyliminopyrine*),



prepared from 4-benzylantipyrinechloride and ammonia, forms yellowish-white crystals melting at 96°, absorbs carbon dioxide from the air, and forms a *hydrochloride* which forms large crystals melting at 217°. The *mercurichloride*, $C_{18}H_{19}N_3,HgCl_2$, crystallises in yellow prisms melting at 129°; the *platinichloride*, $(C_{18}H_{19}N_3)_2,H_2PtCl_6$, is a reddish-yellow precipitate melting at 96°, and passing, on heating, into the salt of 5-aminopyrazole. The *picrate*, $C_{18}H_{19}N_3,C_6H_3O_7N_3$, forms golden-yellow leaflets melting at 147°; the *carbonate* is a white powder melting at 131° and having a strongly alkaline reaction.

The methochloride of 5-chloro-1-phenyl-4-benzylpyrazole (antipyrine chloride) was prepared from the methiodide and silver chloride, and is a hygroscopic powder melting at 148°. When heated with benzoyl chloride in benzene solution, *benzoyl*-4-*benzyliminopyrine* is obtained as crystals melting at 124° and has an alkaline reaction. The *benzenesulphonic* compound forms crystals melting at 141°. 2 : 5-*Methylimino*-1-*phenyl*-2 : 3-*dimethyl*-4-*benzylpyrazole* (4-*benzylmethyliminopyrine*),



is prepared as hydriodide from methyl iodide and 5-methylamino-1-phenyl-3-methyl-4-benzylpyrazole; the *carbonate* forms white crusts with H_2O, melting at 121°.

[With Richard Blume.]—5-*Benzylamino*-1-*phenyl*-3-*methylpyrazole*, $CH\Big\langle{}^{CMe=N}_{C(NAc\cdot C_7H_7)}\Big\rangle NPh$, prepared from antipyrine chloride and benzylamine, is a viscous, yellow oil boiling at 228° under 12 mm. pressure; its *hydrochloride* is microcrystalline powder melting at 159°, and its *platinichloride*, $(C_{17}H_{17}N_3)_2,H_2PtCl_6,H_2O$, forms brownish-red crystals melting at 109°. The *mercurichloride* forms white crystals melting at 129—130°. The acyl derivatives can only be obtained indirectly by heating 2 : 5-benzyliminopyrine with acetyl or benzoyl chloride; the *acetyl* derivative crystallises in leaflets melting at 114° and boiling at 240—245° under 18 mm. pressure; it is basic and forms a *hydrochloride* crystallising in leaflets melting at 203°. The *benzoyl* derivative forms white crystals melting at 121° and boiling at 253° under 18 mm. pressure.

5-*Benzylmethylamino*-1-*phenyl*-3-*methylpyrazole*,

$$CH\Big\langle{}^{CMe=N}_{C(NMe\cdot C_7H_7)}\Big\rangle NPh,$$

prepared from antipyrine chloride and benzylmethylamine, is a viscous yellow oil boiling at 242° under 20 mm. pressure; its *platinichloride* forms reddish-brown crystals melting at 74°. 5-*Dibenzylamino*-1-*phenyl*-3-*methylpyrazole*, prepared by distilling under reduced pressure the benzylchloride of benzyliminopyrine, forms colourless crystals

melting at 106° and boiling at 272° under 18 mm. pressure; the *hydrochloride* forms crystals melting at 148°, and the *platinichloride*, $(C_{24}H_{23}N_3)_2,H_2PtCl_6$, brownish-red prisms melting at 178°.

2:5-*Benzylimino*-1-*phenyl*-2:3-*dimethylpyrazole* (2:5-*benzyliminopyrine*), $\begin{matrix} \text{CMe:NMe} \\ | \quad \text{NPh} \\ \text{CH:C}\text{—} \end{matrix} \Big\rangle \text{N·}C_7H_7$, prepared from antipyrine chloride and benzylamine, is a viscous, yellow oil, strongly basic, absorbing carbon dioxide from the air; its *hydrochloride* is hygroscopic, and its *platinichloride*, $(C_{18}H_{19}N_3)_2,H_2PtCl_6$, forms reddish-brown needles melting at 196°. The *aurichloride* crystallises in brown needles melting at 105°, and the *mercurichloride* white needles melting at 110°; the *carbonate* is hygroscopic, and the *hydriodide*, which is identical with the methiodide from 5-benzylamino-1-phenyl-3-methylpyrazole, crystallises in colourless prisms melting at 159°; the *ferrocyanide* is a white precipitate, and the *picrate* crystallises in yellow leaflets melting at 138·5°.

The *methiodide* of *benzyliminopyrine*, $\text{CH}{<}\begin{matrix}\text{CMe}=\text{NMeI} \\ \text{C(NMe·}C_7H_7)\end{matrix}{>}\text{NPh}$, crystallises in prisms which become yellow in the air and melt at 115°; on heating, methyl iodide is eliminated, and 5-methylbenzylamino-1-phenyl-3-methylpyrazole is formed. The *benzyl chloride* of benzyliminopyrine crystallises in prisms melting at 80°, and the *benzyl iodide* in prisms melting at 158°. The *acetyl iodide*, $\begin{matrix}\text{CMe}=\text{N(MeI)} \\ \text{CH:C(NAc·}C_7H_7)\end{matrix}{>}\text{NPh}$, prepared from the hygroscopic acetyl chloride by potassium iodide, crystallises in prisms melting at 156°; the *benzoyl chloride* forms quadratic crystals melting at 100°, and yields a *platinichloride*, $(C_{25}H_{24}N_3OCl)_2,PtCl_4$, as a pale brown, crystalline powder melting at 206°. The *benzoyl iodide* forms white crystals melting at 51°.

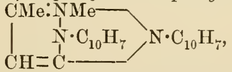
[With Albert Hepner.]—2:5-*Phenylimino*-1-*phenyl*-2:3-*methylpyrazole* (*anilopyrine*), $\begin{matrix} \text{CMe:NMe} \\ | \quad \text{NPh} \\ \text{CH}=\text{C}\text{—} \end{matrix} \Big\rangle \text{NPh}$, prepared by heating the methiodide of 5-chloro-1-phenyl-3-methylpyrazole with aniline at 125° and decomposing the hydriodide with sodium hydroxide, forms crystals melting at 79—80°. Its *acetyl iodide*, prepared from the hygroscopic acetyl chloride, crystallises in needles melting at 204°, the *benzoyl chloride* forms white prisms melting at 214°, and when heated loses methyl iodide, yielding benzoylanilinophenylmethylpyrazole. The *benzoyl iodide* crystallises in prisms melting at 210°. 5-*Benzoylanilino*-1-*phenyl*-3-*methylpyrazole*, $\text{CH}{<}\begin{matrix}\text{CMe}=\text{N} \\ \text{C(NPhBz)}\end{matrix}{>}\text{NPh}$, prepared as just mentioned, melts at 135° and boils at 200° under 16 mm. pressure.

2:5-*Naphthylimino*-1-*phenyl*-2:3-*dimethylpyrazole* (2:5-*naphthyliminopyrine*), $\begin{matrix} \text{CMe:NMe—} \\ | \quad \text{N·}C_{10}H_7 \\ \text{CH}=\text{C}\text{—} \end{matrix} \Big\rangle \text{NPh}$, prepared from antipyrine chloride

and β-naphthylamine, crystallises in greenish-yellow plates melting at 70°, and on heating yields 3-*methylamino*-1-*phenyl*-5-β-*naphthylpyrazole*, which crystallises in brown needles melting at 125°. The *platinichloride* of the naphthyliminopyrine, $(C_{21}H_{19}N_3)_2,H_2PtCl_6$, crystallises in yellow needles melting at 157—163°. The *hydriodide* crystallises in needles melting at 178°. 2 : 5-α-*Naphthylimino*-1-*phenyl*-2 : 3-*dimethylpyrazole* (2 : 5-α-*naphthyliminopyrine*) crystallises in yellowish-green plates or needles melting at 161—162°; its *platinichloride* forms reddish-yellow crystals decomposing at 196—200°; the *hydriodide* forms white crystals melting at 220°, and the *methiodide* needles with H_2O melting at 210°.

[With WILHELM DANZFUSS.]—The *methochloride* of *chloro*-β-*naphthylmethylpyrazole* (β-*naphthylantipyrine chloride*) is prepared from the methiodide and silver chloride, and crystallises in needles melting at 138°; by treatment with aniline, it is converted into 2 : 5-*phenylimino*-1-β-*naphthyl*-2 : 3-*dimethylpyrazole* (1-β-*naphthylanilopyrine*), which crystallises in yellow leaflets melting at 182°; the *platinichloride* forms reddish-brown leaflets melting at 214—215°, and the *hydriodide* white crystals melting at 179°, and the *methiodide* crystals melting at 163°. The *benzoyl chloride* forms hygroscopic crystals, and its *platinichloride*, with H_2O, a red precipitate melting at 242°. The *benzoyl iodide* crystallises in prisms melting and decomposing at 171°. The *acetyl iodide*, prepared from the acetyl chloride, crystallises in white prisms melting at 187°.

5-*Anilino*-1-β-*naphthyl*-3-*methylpyrazole*, prepared from 1-β-naphthylantipyrine chloride and aniline, crystallises in yellow needles melting at 122°. 5-*Benzoylanilino*-1-β-*naphthyl*-3-*methylpyrazole* is not formed on benzoylating the compound last mentioned, but by heating the benzoyl chloride of naphthylanilopyrine, and crystallises in needles melting at 128° and boiling at 265° under 13 mm. pressure. 5-*Methylanilino*-1-β-*naphthyl*-3-*methylpyrazole*, prepared from naphthylantipyrine chloride and methylaniline or by distilling the methiodide of naphthylanilopyrine, crystallises in leaflets melting at 113° and boiling at 245° under 13 mm. pressure; the *platinichloride* crystallises with $2H_2O$ in pale yellow needles melting at 132°. 2 : 5-β-*Naphthylimino*-1-β-*naphthyl*-2 : 3-*dimethylpyrazole* (1-β-*naphthyl*-2 : 5-*naphthyliminopyrine*),



prepared from naphthylantipyrine chloride and naphthylamine, crystallises in dark yellow needles, with $2H_2O$, melting at 68°, and when anhydrous at 122°; the *platinichloride* crystallises with H_2O in leaflets melting and decomposing at 172°. The *hydriodide* of 5-α-naphthylimino-1-β-naphthyl-3-methylpyrazole, from which the free base cannot be isolated, yields, when heated, 5-α-*naphthylamino*-1-β-*naphthyl*-3-*methylpyrazole*, which forms crystals melting at 145°. K. J. P. O.

Bromodihydrouracil. SIEGMUND GABRIEL (*Ber.*, 1905, 38, 1689—1691. Compare this vol., i, 265).—When bromodihydrouracil (Abstr., 1901, i, 294; this vol., i, 266) is boiled with an aqueous solution of sodium sulphite, it is transformed into dihydrouracil, and

when heated with alcoholic ammonia at 100° into uracil. *Thiocyanobromodihydrouracil*, $C_4H_4O_2N_2Br \cdot SCN$, obtained by brominating thiocyanodihydrouracil, crystallises from boiling water in large, four-sided prisms melting and decomposing at 182°.

2 : 6-*Dichloropyrimidine*, $CCl{<}{\begin{smallmatrix}N-CH\\N:CCl\end{smallmatrix}}{>}CH$, obtained by the action of phosphorus oxychloride on uracil at 140°, distils at 208·5—209·5° under 773 mm. pressure, crystallises from light petroleum in compact needles, melts at 61°, and volatilises in the air. When heated with alcoholic ammonia at 100° for 2 hours, the chloro-base yields 2-amino-6-chloropyrimidine (Gabriel and Colman, Abstr., 1904, i, 103) and 6-*amino-2-chloropyrimidine*. The latter crystallises from ethyl acetate in compact prisms, melts at 206—207°, and sublimes when carefully heated on a watch-glass. J. J. S.

Pyrimidines. VIII. Structure of Certain Derivatives. HENRY L. WHEELER and H. STANLEY BRISTOL (*Amer. Chem. J.*, 1905, **33**, 437—448).—The following compounds have been prepared by the action of alkyl bromides on thiocarbamide. *ψ-Propylthiocarbamide hydrobromide* crystallises in long, colourless needles and melts at about 60°. *ψ*-iso*Butylthiocarbamide hydrobromide* forms a fibrous mass of crystals and melts at about 96°. *ψ*-iso*Amylthiocarbamide hydrobromide* crystallises in long prisms and melts at about 84°.

The following substances have been obtained by the method described for the preparation of 6-oxy-2-methylthiolpyrimidine (Abstr., 1903, i, 524). 6-*Oxy-2-propylthiolpyrimidine*, $NH{<}{\begin{smallmatrix}C(SPr^a):N\\CO\text{——}CH\end{smallmatrix}}{>}CH$, crystallises in long, colourless needles, melts at 117°, and is readily soluble in alcohol or hot water. 6-*Oxy*-2-iso*butylthiolpyrimidine* forms leaf-like plates and melts at 107°. 6-*Oxy*-2-iso*amylthiolpyrimidine* crystallises in long, thin plates and melts at 115°.

[With SAMUEL H. CLAPP.]—When uracil is heated at 125° with a mixture of concentrated sulphuric and fuming nitric acids, 5-nitrouracil is obtained.

By the reduction of 5-nitrouracil with aluminium amalgam, 5-aminouracil is produced; its picrate melts and decomposes at 247—248°, and not at 147°, as stated by Behrend and Grünwald (Abstr., 1900, i, 63).

By the action of a mixture of concentrated nitric and sulphuric acids on 6-oxy-2-ethylthiolpyrimidine, 5-nitrouracil is produced. When 6-oxy-2-thiopyrimidine is treated with nitric acid, 5-nitrouracil is formed, together with another substance, which is probably 6-oxypyrimidine.

[By TREAT B. JOHNSON.]—Nitrouracil is also produced when 6-chloro-2-ethylthiolpyrimidine is treated with a mixture of nitric and sulphuric acids.

When 5-bromouracil is warmed with a mixture of phosphorus pentachloride and phosphorus oxychloride, 2 : 6-*dichloro-5-bromopyrimidine*, $N{<}{\begin{smallmatrix}CCl=N\\CCl \cdot CBr\end{smallmatrix}}{>}CH$, is produced, which boils at 119—120° under 17—18 mm. pressure, and on cooling solidifies to a crystalline

mass and melts at about $-3°$; by the action of aniline on this compound, 5-*bromo*-2 : 6-*dianilinopyrimidine*, $N{<}\genfrac{}{}{0pt}{}{C(NHPh)=N}{C(NHPh)\cdot CBr}{>}CH$, is formed, which crystallises in colourless needles, melts at 191°, and is sparingly soluble in water.

5-*Bromo*-6-*oxy*-2-*anilinopyrimidine*, $NH{<}\genfrac{}{}{0pt}{}{C(NHPh):N}{CO\text{———}CBr}{>}CH$, obtained by the action of aniline on 6-oxy-5-bromo-2-ethylthiolpyrimidine, crystallises in colourless needles, melts and decomposes at 246°, and is sparingly soluble in water, alcohol, benzene, or acetone; when this substance is heated with phosphorus oxychloride, 6-*chloro*-5-*bromo*-2-*anilinopyrimidine*, $N{<}\genfrac{}{}{0pt}{}{C(NHPh):N}{CCl\text{——}CBr}{>}CH$, is produced, which crystallises in long, radiating, colourless needles, melts at 106—107°, is readily soluble in ether or benzene, and is converted by aniline into 5-bromo-2 : 6-dianilinopyrimidine.

6-*Oxy*-2-*ethylthiol*-4-*ethylpyrimidine*, $NH{<}\genfrac{}{}{0pt}{}{C(SEt):N}{CO\text{—}CH}{>}CEt$ crystallises in colourless, transparent prisms, melts at 89°, and is very soluble in alcohol and slightly so in hot water; when this substance is treated with bromine, it is converted into 5-*bromo*-6-*oxy*-2-*ethylthiol*-4-*ethylpyrimidine*, $NH{<}\genfrac{}{}{0pt}{}{C(SEt):N}{CO\text{—}CBr}{>}CEt$, which crystallises from alcohol in colourless, transparent prisms and melts at 172—173·5°. By the action of hot concentrated hydrochloric acid on 6-oxy-2-ethylthiol-4-ethylpyrimidine or its bromo-derivative, 4-*ethyluracil*, $NH{<}\genfrac{}{}{0pt}{}{CO\cdot NH}{CO\cdot CH}{>}CEt$, is obtained, which crystallises from alcohol in colourless tables, melts at 204°, effervesces at about 270°, and is readily soluble in water. 5-*Bromo*-4-*ethyluracil*, $NH{<}\genfrac{}{}{0pt}{}{CO\text{—}NH}{CO\cdot CBr}{>}CEt$, crystallises in prisms or plates, melts at 230—231°, and is slightly soluble in hot water.

6-*Oxy*-2-*methylthiolpyrimidine hydrochloride* melts and decomposes at 189°, and when warmed with a mixture of phosphorus pentachloride and phosphorus oxychloride is converted into 6-*chloro*-2-*methylthiolpyrimidine*, $N{<}\genfrac{}{}{0pt}{}{C(SMe):N}{CCl\text{—}CH}{>}CH$, which is obtained as a colourless oil boiling at 139—140° under 36 mm. pressure; it solidifies on cooling and melts at from $-2°$ to $-0°$. When this chloro-derivative is heated with alcoholic ammonia, 6-*amino*-2-*methylthiolpyrimidine*, $N{<}\genfrac{}{}{0pt}{}{C(SMe)=N}{C(NH_2)\cdot CH}{>}CH$, is formed, which crystallises in colourless, prismatic plates, melts at 125—126°, and is readily soluble in alcohol or acetone. E. G.

Pyrimidines: Action of Potassium Thiocyanate on Certain Imide Chlorides. IX. Henry L. Wheeler and H. Stanley Bristol (*Amer. Chem. J.*, 1905, **33**, 448—460).—2-*Ethylthiol*-6-*thiocarbimidopyrimidine*, $N{<}\genfrac{}{}{0pt}{}{C(SEt)=N}{C(NCS)\cdot CH}{>}CH$, obtained by the action of potassium thiocyanate on a solution of 6-chloro-2-ethylthiolpyrimidine

in toluene, boils at 180° under 32 mm. pressure, solidifies on cooling, crystallises from benzene in pale yellow, prismatic plates, and melts at 175°. When this compound is treated with ammonia, *2-ethylthiol-6-thiocarbamidopyrimidine*, $N{<}\genfrac{}{}{0pt}{}{C(SEt)=\!=\!=\!=\!=N}{C(NH\cdot CS\cdot NH_2)\cdot CH}{>}CH$, is produced, which crystallises from alcohol in long, thin, colourless prisms, melts at 214°, and is sparingly soluble in water. By the action of aniline on 2-ethylthiol-6-thiocarbimidopyrimidine, *2-ethylthiol-6-phenylthiocarbamidopyrimidine* is formed, which crystallises in long, colourless needles, melts at 205°, and is fairly soluble in hot alcohol, but almost insoluble in hot water.

Ethyl 2-ethylthiolpyrimidine-6-thioncarbamate,

$$N{<}\genfrac{}{}{0pt}{}{C(SEt)=\!=\!=\!=\!=N}{C(NH\cdot CS\cdot OEt)\cdot CH}{>}CH,$$

obtained by the action of an alcoholic solution of potassium thiocyanate on 6-chloro-2-ethylthiolpyrimidine, crystallises in long, thin, light yellow plates, melts at 93°, is readily soluble in hot alcohol, and is decomposed by hot concentrated hydrochloric acid with formation of uracil and cytosine.

2-Ethylthiol-6-thiocarbamido-5-methylpyrimidine,

$$N{<}\genfrac{}{}{0pt}{}{C(SEt)=\!=\!=\!=\!=N}{C(NH\cdot CS\cdot NH_2)\cdot CMe}{>}CH,$$

obtained by the action of potassium thiocyanate on 6-chloro-2-ethylthiol-5-methylpyrimidine in presence of toluene, crystallises in radiating needles, melts at 192°, and is fairly soluble in hot alcohol or benzene and sparingly so in hot water. When the reaction mixture is boiled with alcohol, *ethyl 2-ethylthiol-5-methylpyrimidine-6-thioncarbamate*,

$$N{<}\genfrac{}{}{0pt}{}{C(SEt)=\!=\!=\!=\!=N}{C(NH\cdot CS\cdot OEt)\cdot CMe}{>}CH,$$

is produced, which crystallises in pale yellow prisms, melts at 88—89°, and is readily soluble in alcohol, ether, or benzene and sparingly so in water.

6-Chloro-5-bromo-2-ethylthiolpyrimidine (Wheeler and Johnson, Abstr., 1904, i, 624) boils at 168° under 24—25 mm. and at 179—180° under 36 mm. pressure. By the action of potassium thiocyanate on a solution of this substance in toluene, *5-bromo-2-ethylthiol-6-thiocarbimidopyrimidine*, $N{<}\genfrac{}{}{0pt}{}{C(SEt)=\!=\!=N}{C(NCS)\cdot CBr}{>}CH$, is formed, which crystallises in small, pale yellow prisms, melts at 79—80°, and is readily soluble in benzene or toluene and sparingly so in light petroleum. If alcoholic ammonia is added to the reaction mixture, *5-bromo-2-ethylthiol-6-thiocarbamidopyrimidine* separates, which crystallises in light yellow plates, melts at 220°, and is sparingly soluble in water or alcohol, but more soluble in benzene. When the thiocarbimide compound is treated with aniline, *5-bromo-2-ethylthiol-6-phenylthiocarbamidopyrimidine* is obtained, which crystallises from alcohol in slender, colourless needles, melts at 166—167°, and is fairly soluble in benzene.

When 6-chloro-5-bromo-2-ethylthiolpyrimidine is heated with an alcoholic solution of potassium thiocyanate, ethyl 5-bromo-2-ethylthiolpyrimidine-6-thioncarbamate is produced, together with 5-bromo-6-thio-2-ethylthiolpyrimidine and 5-bromo-6-amino-2-ethylthiolpyrimidine.

Ethyl 5-*bromo*-2-*ethylthiolpyrimidine*-6-*thioncarbamate*,

$$\mathrm{N}\Big<\begin{matrix}\mathrm{C(SEt)}\!=\!=\!=\!=\!=\!=\!=\!=\mathrm{N}\\ \mathrm{C(NH\cdot CS\cdot OEt)\cdot CBr}\end{matrix}\Big>\mathrm{CH},$$

crystallises in long, pointed, light yellow, prismatic plates, melts at 82°, and is readily soluble in hot alcohol. 5-*Bromo*-6-*thio*-2-*ethylthiolpyrimidine*, $\mathrm{NH}\Big<\begin{matrix}\mathrm{C(SEt){:}N}\\ \mathrm{CS-CBr}\end{matrix}\Big>\mathrm{CH}$, forms pale yellow plates, and melts and decomposes at 198°; this compound can also be prepared by the action of potassium hydrogen sulphide on 6-chloro-5-bromo-2-ethylthiolpyrimidine. When ethyl 5-bromo-2-ethylthiolpyrimidine-6-thioncarbamate is treated with ethyl bromide in presence of sodium ethoxide, *ethyl* 5-*bromo*-2-*ethylthiolpyrimidine*-6-*iminothiocarbonate*, $\mathrm{N}\Big<\begin{matrix}\mathrm{C(SEt)}\!=\!=\!=\!=\!=\!=\!=\!=\mathrm{N}\\ \mathrm{C[N{:}C(SEt)\cdot OEt]\cdot CBr}\end{matrix}\Big>\mathrm{CH}$, is formed, which crystallises in long, colourless prisms, melts at 43°, and is readily soluble in alcohol or ether; if ammonia is passed into an alcoholic solution of this compound, 5-*bromo*-2-*ethylthiol*-6-ψ-*ethylcarbamidopyrimidine*,

$$\mathrm{N}\Big<\begin{matrix}\mathrm{C(SEt)}\!=\!=\!=\!=\!=\!=\!=\!=\mathrm{N}\\ \mathrm{C[N{:}C(NH_2)\cdot OEt]\cdot CBr}\end{matrix}\Big>\mathrm{CH},$$

is obtained, which crystallises from alcohol in long needles, melts at 110°, decomposes at 230°, is readily soluble in benzene or warm alcohol, and sparingly so in hot water. When a solution of this ψ-carbamidopyrimidine in benzene is heated with sodium, 5-*bromo*-2-*ethylthiol*-6-*cyanoamidopyrimidine* is produced. This compound is converted by concentrated hydrochloric acid into 5-*bromo*-2-*ethylthiol*-6-*carbamidopyrimidine*, $\mathrm{N}\Big<\begin{matrix}\mathrm{C(SEt)}\!=\!=\!=\!=\!=\!=\!=\mathrm{N}\\ \mathrm{C(NH\cdot CO\cdot NH_2)\cdot CBr}\end{matrix}\Big>\mathrm{CH}$, which crystallises from alcohol and melts at 167°; if the carbamidopyrimidine is heated at 170—180°, 5-bromo-6-amino-2-ethylthiolpyrimidine is formed, whilst by the action of boiling concentrated hydrochloric acid it is converted into 5-bromocytosine (Abstr., 1904, i, 625).

2-*Thiouracil*, $\mathrm{NH}\Big<\begin{matrix}\mathrm{CS\cdot NH}\\ \mathrm{CO\cdot CH}\end{matrix}\Big>\mathrm{CH}$, obtained by the action of ethyl sodioformylacetate on thiocarbamide, crystallises in colourless prisms and decomposes above 300°.

6-*Anilino*-2-*ethylthiolpyrimidine hydrochloride*, produced by the action of aniline on 6-chloro-2-ethylthiolpyrimidine, melts and decomposes at 198°; the corresponding *base* crystallises in colourless needles, melts at 68°, and is very soluble in alcohol. When the hydrochloride is boiled with strong hydrochloric acid, 2-*oxy*-6-*anilinopyrimidine* (*phenylcytosine*) *hydrochloride*, $\mathrm{N}\Big<\begin{matrix}\mathrm{CO}\!-\!-\!-\!-\mathrm{NH}\\ \mathrm{C(NHPh)\cdot CH}\end{matrix}\Big>\mathrm{CH,HCl}$, is obtained, which decomposes at 228°; the *base* crystallises in colourless, six-sided plates, melts at about 269°, and is fairly soluble in hot alcohol; the *platinichloride* crystallises with $1H_2O$.

2 : 6-*Dianilinopyrimidine*, $\mathrm{N}\Big<\begin{matrix}\mathrm{C(NHPh)}\!=\!\mathrm{N}\\ \mathrm{C(NHPh)\cdot CH}\end{matrix}\Big>\mathrm{CH}$, prepared by heating 6-chloro-2-ethylthiolpyrimidine (1 mol.) with aniline (2 mols.), crystallises from alcohol in six-sided plates, melts at 136—137°, and is fairly soluble in hot benzene or ether; the *hydrochloride* melts at 197°.

2-*Ethylthiol*-5-*phenyluracil*, $\mathrm{NH}\Big<\begin{matrix}\mathrm{C(SEt){:}N}\\ \mathrm{CO-CPh}\end{matrix}\Big>\mathrm{CH}$, obtained by the

condensation of sodium phenylformylethylacetate with the additive compound of thiocarbamide with ethyl iodide, crystallises in long needles, melts at 158°, and is readily soluble in alcohol or hot water. When this compound is heated with concentrated hydrochloric acid, it is converted into 5-*phenyluracil*, $NH<\substack{CO-NH \\ CO\cdot CPh}>CH$, which forms microscopic plates and does not melt below 350°. E. G.

Action of Nitric Acid on Aminosulphonic Acids; Nitro-amines, Diazo-compounds, and Indazoles. THEODOR ZINCKE (*Annalen*, 1905, **339**, 202—241).—Although the action of nitric acid on aminosulphonic acids has been investigated, so far only nitrodiazobenzenesulphonic acids have been observed as the products of the reaction. It has been found that *m*-aminobenzenesulphonic acids yield nitrodiazobenzenesulphonic acids, whilst the *o*- and *p*-aminobenzenesulphonic acids yield nitrated nitroaminobenzenes together with diazo-salts. In the case of the two classes of compounds last mentioned, the sulphonic groups are first replaced by nitro-groups, and these stable nitroanilines then converted into nitroamines. In the *m*-compounds, the sulphonic acid group is not replaced, and consequently oxidation takes place, nitrous acid is formed, and then the amine converted into diazo-compound.

When a methyl group is in the ortho-position with respect to the nitroamino-group, indazoles are formed.

[With E. ELLENBERGER.]—When *p*-xylidinesulphonic acid is added to pure nitric acid at $-5°$, 3 : 5-*dinitro*-2-*nitroamino*-p-*xylene*,

$$C_6HMe_2(NO_2)_2\cdot NH\cdot NO_2,$$

is obtained as colourless needles melting and decomposing at 130°; when boiled with phenol, it is converted into the corresponding dinitroxylidine; the *potassium*, *sodium*, and *silver* salts form needles. By nitrous acid, the nitroamine is converted into the *nitrodiazo-xylene*, which is also formed as a by-product in the action of the nitric acid on the sulphonic acid; the diazo-compound forms a coupled product with dimethylaniline, $C_{16}H_{17}O_4N_5$, which crystallises in reddish-brown leaflets melting at 220°; a *perbromide* was prepared. When boiled in aqueous solution, 5 : 7-*dinitro*-6-*methylindazole*,

$$C_6HMe(NO_2)_2<\substack{CH \\ | \\ N}>NH,$$

is obtained as colourless needles melting at 228°; it is also formed directly from the sulphonic acid by diluting with water after treatment with nitric acid and boiling; the *sodium* salt crystallises in reddish-yellow needles, and the *silver* salt is a pale yellow, crystalline powder. The *acetyl* compound crystallises in plates melting at 185°.

3 : 5-*Dichloro*-p-*xylene*-2-*diazonium perchloride*, $C_6HCl_2Me_2\cdot N_2Cl_3$, is obtained when a solution of the nitroamine in acetyl chloride or chloroform is treated with chlorine, and crystallises in leaflets or needles melting at 120°; by treatment with potassium bromide, the *perbromide* is formed, crystallising in pale yellow needles decomposing at 155°. The *platinichloride*, $C_{16}H_{14}N_4Cl_6,PtCl_4$, forms pale yellowish-brown leaflets melting and decomposing at 159°. Very explosive per-

manganates and perchlorates can be prepared from the perchloride. Dimethylaniline and the perchloride give the *compound*

$$NMe_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6HCl_2Me_2$$

as orange-red needles melting at 121°; the β-naphthol *derivative* crystallises in red needles melting at 195°.

[With A. MAUÉ.]—The *m*-xylidinesulphonic acid

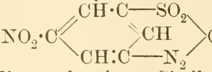
$$[Me_2 : NH_2 : SO_3H = 1 : 3 : 4 : 6]$$

and nitric acid yield, not a nitroamine but 2-*nitro*-4-*diazo-xylene*-6-*sulphonic acid*, which crystallises in needles exploding on heating; with dimethylaniline it yields a dimethylaniline *salt* of a dimethylanilineazonitro-xylenesulphonic acid, which crystallises in red needles unchanged at 200°; the *ammonium* salt forms dark red needles. The free *acid* crystallises in reddish-yellow needles unchanged at 250°. The β-naphthylamine *salt* of the naphthylamineazonitro-xylenesulphonic acid crystallises in deep red needles, and the *ammonium* in red needles. The free *acid* forms dark red needles.

[With PH. MALKOMESIUS.]—The main product of the action of nitric acid on *o*-toluidine-5-sulphonic acid is 3 : 5-*dinitro*-2-*nitroaminotoluene*, which forms yellow, explosive crystals melting at 92°. The *sodium* salt crystallises in yellow leaflets or needles, the *barium* salt in yellow leaflets, and the *silver* salt is a yellow, crystalline powder. With nitrous acid, the nitroamine yields a diazo-compound, with tin and hydrochloric acid a triaminotoluene, with chlorine and acetyl chloride a chlorinated diazo-compound, and with bleaching powder a tetranitroazotoluene. The sodium salt of the nitroamine and methyl iodide yield the N-*methyl* ester, which forms brass-yellow crystals melting at 119°; the O-*ester* is obtained from the silver salt, and crystallises in yellow plates melting at 72—73°. Phenol converts the nitroamine into 3 : 5-dinitro-*o*-toluidine. 2 : 4 : 2′ : 4′-*Tetranitro*-o-*azotoluene* is formed when bleaching powder solution is added to a solution of the sodium salt of the nitroamine in methyl alcohol and acetic acid added; it crystallises in yellowish-red needles melting and decomposing at 218°. 3 : 5-*Dinitrotoluene*-2-*diazonium nitrate* is obtained as a by-product in the preparation of the nitroamine, and is converted into a β-*naphthylamine* derivative, which crystallises in reddish-brown needles melting at 117°; the *perbromide* is a pale red, crystalline powder exploding at 64°. With ammonia it yields 3 : 5-*dinitrotoluenediazoimide*, and, when boiled with alcohol, 2-*bromo*-3 : 5-*dinitrotoluene*, which forms yellow crystals melting at 91—92°. 5 : 7-*Dinitroindazole*, $\begin{array}{l} C(NO_2){\cdot}CH{:}C{\cdot}CH \\ CH{\cdot}C(NO_2){:}C{\cdot}N \end{array}\!\!>\!NH$, prepared by boiling an aqueous solution of the diazonium salt, crystallises in yellow needles melting at 215°; the *sodium* salt forms yellowish-red needles; the *silver* salt is a yellow, crystalline precipitate, and the *acetyl* derivative forms yellow needles melting at 196°.

[With A. KUCHENBECKER.]—At a low temperature, sulphanilic acid gives 2 : 4-dinitroaniline and at a higher temperature diazobenzene-*p*-sulphonic acid. 2 : 6-Dibromosulphanilic acid yields 2 : 6-*dibromo*-4-*nitro*-1-*nitroaminobenzene*, a greyish-white, crystalline powder, exploding on heating. 2 : 4-*Dinitro*-1-*nitroaminobenzene* is formed from *o*-nitrosulphanilic acid at − 15° and is a colourless, crystalline powder

melting and decomposing at 101°. *p*-Toluidine-5-sulphonic acid yields 3 : 5-*dinitro*-4-*nitroaminotoluene*, which forms colourless crystals melting and decomposing at 104°. The silver salt forms brass-yellow crystals.

m-Sulphanilic acid is converted by nitric acid into 3-*nitrodiazobenzene*-5-*sulphonic acid*,  which is a yellowish-white powder exploding on heating. Similarly, 2 : 6-dibromo-*m*-sulphanilic acid yields 2 : 6-*dibromo*-3-*nitrodiazobenzene*-5-*sulphonic acid*, a yellow, explosive, crystalline powder. From *p*-toluidine-6-sulphonic acid, 2-*nitro*-p-*diazotoluene*-6-*sulphonic acid* is obtained as thick, yellow, explosive crystals. *o*-Toluidine-4-sulphonic acid yields 3 : 5-*dinitro*-o-*diazotoluene*-4-*sulphonic acid*, which forms colourless crystals becoming brown in the air and exploding on heating. When boiled with acids, it passes into 5 : 7-*dinitroindazole*-6-*sulphonic acid*, which crystallises in colourless needles; the *silver* salt, $C_7H_3O_7N_4SAg,H_2O$, crystallises in yellow plates and yields with excess of silver nitrate the *salt*

$$C_7H_2O_7N_4SAg_2,$$

which is a brass-yellow, crystalline powder. The *potassium* and *ammonium* salts crystallise with $2H_2O$ in colourless needles. When the *sodium* salt is heated with concentrated sodium hydroxide, 5 : 7-*dinitro*-6-*hydroxyindazole*, $C_7H_4O_5N_4$, is formed as brass-yellow needles melting at 232—233°; with sodium carbonate, it yields a phenolic *sodium* salt, which is yellow, and with sodium hydroxide the *disodium* salt, which is deep red, but hydrolysed by water into the yellow salt. Ammonia gives only one salt. The *diacetyl* derivative, $C_{11}H_8O_7N_4$, crystallises in needles melting at 195°. When boiled with ammonia, 5 : 7-*dinitro*-6-*aminoindazole* is formed, and crystallises in brownish-yellow scales melting above 270°. The *diacetyl* compound crystallises in needles melting and decomposing at 182°. Aniline converts the indazolesulphonic acid into 5 : 7-*dinitro*-6-*anilinoindazole*, $C_{13}H_9O_4N_5$, which forms red crystals; other bases yield similar compounds. K. J. P. O.

Condensation of Flavinduline with Methylene Compounds. II. Franz Sachs and Guido Bargellini (*Ber.*, 1905, **38**, 1742—1745. Compare Abstr., 1899, i, 239).—Flavinduline hydrobromide condenses with ethyl acetoacetate in alcoholic solution in the presence of sodium hydroxide to form the *compound* $C_{32}H_{24}O_3N_2$, which separates from a mixture of benzene and light petroleum as a dark blue powder and melts at 205—206°. Its solution in acetic acid is orange-red, and with nitric acid it forms a dark red oil. When hydrogen chloride is passed into the solution of the condensation product in toluene, a violet-red powder separates from the alcoholic solution, of which the *platinichloride*, $C_{64}H_{50}O_4N_4Cl_6Pt$, was prepared.

The condensation *product*, $C_{34}H_{21}N_3$, prepared from flavinduline and benzyl cyanide, forms dark green crystals and melts at 240—241°. With glacial acetic acid it forms a green solution, and with concentrated sulphuric acid a cherry-red solution.

The condensation *product*, $C_{31}H_{22}O_2N_2$, formed from flavinduline and

acetylacetone, is an olive-green powder and melts at 240—245°. Its solution in acetic acid is brownish-yellow. Its solution in concentrated sulphuric acid is cherry-red.

The condensation *product*, $C_{33}H_{26}O_4N_2$, prepared from flavinduline and ethyl malonate, forms dark green crystals with a violet lustre. With alcohol, glacial acetic acid, and concentrated sulphuric acid respectively, its solutions are greenish-blue, olive-green, and cherry-red respectively.

The condensation *product*, $C_{31}H_{21}O_2N_3$, prepared from flavinduline and ethyl cyanoacetate, forms dark green crystals with a violet lustre. It forms a bluish-green solution with ethyl alcohol and glacial acetic acid respectively, whilst its solution in concentrated sulphuric acid is red.

The condensation *product*, $C_{29}H_{16}N_4$, prepared from flavinduline and malononitrile, forms dark green crystals with a violet lustre. Its solution in glacial acetic acid is green, and in concentrated sulphuric acid red. A. McK.

Condensation of Form*iso*butaldol with Dimethylaniline. Maximilian Samec (*Monatsh.*, 1905, **26**, 391—411. Compare Wessely, Abstr., 1900, i, 428).—When heated together with zinc chloride at 130°, form*iso*butaldol and dimethylaniline react yielding the *leuco*-base, $NMe_2\cdot C_6H_4\cdot CH_2\cdot CMe_2\cdot CH(C_6H_4\cdot NMe_2)_2$, which forms colourless crystals, melts at 94—95°, or sometimes at 85°, is easily soluble in alcohol, ether, benzene, light petroleum, or dilute acids, and forms crystalline salts; the *oxalate* and the *hydrochloride* are colourless; the *platinichloride* is brown. On oxidation of the leuco-base with lead peroxide, the carbinol and its anhydride are formed; these are precipitated with zinc chloride and treated with ammonia, when the *carbinol*, $C_{29}H_{39}ON_3$, is obtained in colourless crystals. On warming, or in a vacuum at the laboratory temperature, this loses water and forms the *anhydride*, $C_{29}H_{37}N_3$, as a brittle, blue mass, which is reduced by zinc and hydrochloric acid to the leuco-base. The *oxalate*, $C_{29}H_{37}N_3,3C_2H_2O_4$, is hygroscopic; the *zincochloride*, $C_{29}H_{37}N_3,2ZnCl_2$, dyes animal fibres directly, vegetable fibres when mordanted; the *tetrahydrochloride*, $C_{29}H_{37}N_3,4HCl$, is hygroscopic, softens at 55°, gradually evolves hydrogen chloride, and melts at 101—103°; the green *trihydrochloride*, $C_{29}H_{37}N_3,3HCl$, melts at about 150°. When fused, the dye and its salts are dark blue with red fluorescence; the alcoholic solution of the dye and the very dilute aqueous or moderately dilute alcoholic solutions of the salts are reddish-blue, whilst the concentrated aqueous or moderately acid solutions of the salts are green. The differences have been studied spectrophotometrically and the results expressed in curves typical of the different states. Measurements of the electrical conductivity of solutions of various concentrations of the trihydrochloride show that the change from green to blue on dilution is accompanied by a change in the molecular conductivity.

When heated with sodium ethoxide in absolute alcoholic solution, the tetrahydrochloride of the dye forms the *ethyl* ether of the carbinol, $C_{29}H_{38}N_3\cdot OEt$, which separates in scarlet crystals and melts at 65°.

On treatment with aqueous potassium hydroxide, the salts of the dye are gradually converted into the carbinol; the velocity of the change can be measured by the diminution of the electrical conductivity of the solution. G. Y.

Reduction of Derivatives of Carboxylic Acids to Derivatives of Aldehydes. II. FRANZ HENLE (*Ber.*, 1905, **38**, 1362—1369).—The reduction of imino-ethers dissolved in a mineral acid by sodium amalgam in presence of phenylhydrazine or a similar substance (Abstr. 1902, i, 790) probably occurs through the intermediate formation of an additive compound, thus:

$$\mathrm{OEt{\cdot}CR(NH{\cdot}NR'R''){\cdot}NH_2,HCl}$$

$$\swarrow_{\mathrm{-EtOH}} \qquad\qquad \searrow^{\mathrm{-NH_4Cl}}$$

$$\underset{\text{Hydrazidine.}}{\mathrm{HCl,NH_2{\cdot}CR{:}N{\cdot}NR'R''}} \xrightarrow[\mathrm{-NH_4Cl}]{\mathrm{+H_2}} \underset{\text{Hydrazone.}}{\mathrm{CHR{:}N{\cdot}N{\cdot}R'R''}} \xleftarrow[\mathrm{-EtOH}]{\mathrm{+H_2}} \underset{\text{Hydrizino-ether.}}{\mathrm{OEt{\cdot}CR{:}N{\cdot}NR'R''}}$$

Using acetic acid in the reduction in place of a mineral acid, a hydrizino-ether separates. The bases available for the reduction are semicarbazide, phenylhydrazine (not in all cases), phenylmethyl-, diphenyl-, and phenylbenzyl-hydrazines. The following do not give a favourable result: piperyl- and benzyl-hydrazines, aniline, *p*-toluidine, mesidine, *a*-naphthylamine, *ac*-tetrahydro-*β*-naphthylamine, benzidine. Sodium amalgam cannot be replaced by any other reducing agent.

The following reductions are described: *p*-tolimino-ether to *p*-tolualdehyde phenylhydrazone; phenylacetimino-ether to phenylacetaldehydephenylhydrazone and the following derivatives: (1) *phenylacetaldehydediphenylhydrazone*, $CH_2Ph\cdot CH{:}N\cdot NPh_2$, separates from alcohol in colourless crystals and melts at 101—102°; (2) *phenylacetaldehydephenylbenzylhydrazone* crystallises from alcohol in colourless needles and melts at 80—81°; (3) *phenylacetaldehydesemicarbazone* separates from ethyl acetate as a heavy, white, crystalline powder and melts at 156°. Succinimino-ether gives the following substances with different hydrazines: *succinaldehydebisdiphenylhydrazone*,

$$C_2H_4(CH{:}N\cdot NPh_2)_2,$$

crystallises from alcohol in long, colourless needles and melts at 120°; *succinaldehydebisphenylmethylhydrazone*, $C_2H_4(CH{:}N\cdot NMePh)_2$, crystallises from light petroleum in colourless prisms and melts at 86°; *succinaldehydebisphenylbenzylhydrazone* crystallises from light petroleum and melts at 147—148°.

Phenylacetophenylhydrizinoether, $CH_2Ph\cdot C(OEt){:}N\cdot NHPh$, is prepared from phenylacetimino-ether hydrochloride by treatment with magnesium powder and phenylhydrazine in cold 4 per cent. acetic acid solution; it crystallises from heavy petroleum in long, colourless needles, melts at 76°, and when distilled with steam after adding oxalic acid gives ethyl phenylacetate. W. A. D.

Hydroxydiphenyltriazine and Hydroxydiphenyldihydrotriazine. Heinrich Biltz (*Ber.*, 1905, **38**, 1417—1419).—3-Hydroxy-5 : 6-diphenyl-1 : 2 : 4-triazine (Thiele, Abstr., 1895, i, 251) is best prepared by the interaction of benzil and semicarbazide hydrochloride in glacial acetic acid solution ; it boils at 224—225°. The corresponding *hydroxy-triazine* derivative from anisil melts at 261—262°, that from piperil at 248°, and that from cuminil at 250°. *Hydroxydiphenyldihydrotriazine*, prepared by the reduction of the foregoing compound with zinc shavings and acetic acid, crystallises in colourless needles and melts at 275—276°. The corresponding *dihydro*-compound from anisil melts at 212—213°, that from piperil at 285°, and that from cuminil at 255—256°. E. F. A.

A Reaction of Secondary Amines. Angelo Angeli and Vincenzo Castellana (*Atti R. Accad. Lincei*, 1905, [v], **14**, i, 272—277. Compare Angeli, Abstr., 1901, i, 57, and Angeli and Angelico, Abstr., 1901, i, 322).—It has been shown (*loc. cit.*) that nitroxyl, which is probably an anhydride of dihydroxyammonia, readily reacts with secondary amines, $NHRR^1$, giving rise to tetrazones when R and R^1 are aliphatic residues or to diazo-compounds when R is an aromatic group and R^1 hydroxyl.

When molecular proportions of piperidine hydrochloride and sodium nitrohydroxylaminate are heated together in concentrated aqueous solution, the following compounds are formed : (1) the piperylhydrazine, $C_5H_{12}N_2$, obtained by Knorr by reducing the corresponding nitrosoamine (Abstr., 1884, 467). (2) *Dipiperylhydrazine*,

$$C_5NH_{10}\cdot NH\cdot NH\cdot C_5NH_{10},$$

which separates from water in large, colourless crystals melting at 98°, readily reduces Fehling's solution, and reacts with benzoyl chloride, potassium cyanate, and benzaldehyde. Its formation is probably due to the action of piperylhydrazine on the hydroxypiperylhydrazine doubtless formed in the first phase of the reaction :

$$C_5NH_{10}\cdot NH\cdot OH + C_5NH_{10}\cdot NH_2 = C_5NH_{10}\cdot NH\cdot NH\cdot C_5NH_{10} + H_2O.$$

It yields a *picrate*, $(C_5H_{11}N)_2,2C_6H_3O_7N_3$, which crystallises from alcohol in yellow needles, melting and decomposing at 175°. (3) Piperyltetrazone, $C_{10}H_{20}N_4$, obtained by oxidising piperylhydrazine by means of mercuric oxide (Abstr., 1882, 1115, and 1884, 467). (4) A *compound*, $C_{10}H_8N_4$, probably having the constitution

$$\begin{array}{l}CH_2\cdot CH_2\cdot N\cdot NH\cdot NH\cdot N\cdot CH_2\cdot CH_2\\ \,|\qquad\qquad\;\;|\qquad\qquad\qquad\;|\qquad\qquad\;|\\ CH_2\cdot CH_2\cdot C=\!=\!=\!=\!=\!=C\cdot CH_2\cdot CH_2\end{array},$$

which separates from light petroleum in large, colourless crystals melting at 154°. It may be obtained in a purer state by oxidising the original mixture with mercuric oxide. It reduces Fehling's solution and yields a benzoyl derivative and a *picrate*, $C_{10}H_{18}N_4,2C_6H_3O_7N_3$, melting at 174°. T. H. P.

Derivative of Glycuronic Acid and *p*-Nitrophenylhydrazine. An. K. Medvedeff (*Ber.*, 1905, **38**, 1646—1650).—The action of a solution of *p*-nitrophenylhydrazine on a solution of glycuronic acid, almost saturated with sodium acetate and rendered faintly alkaline with sodium carbonate, yields a *compound*, $C_{18}H_{22}O_5N_6$, which crystal-

lises from dilute alcohol in flat, monoclinic (?) prisms melting and decomposing at 125°. The compound is of the hydrazone-hydrazide or osazone type, and contains the *p*-nitrophenylhydrazine in a reduced state; its constitution is expressed by

$$NH_2\cdot C_6H_4\cdot NH\cdot N\colon CH\cdot C(N\cdot NH\cdot C_6H_4\cdot NH_2)\cdot [CH\cdot OH]_3\cdot CO_2H, \text{ or}$$

$$OH\cdot CH_2\cdot C\leqslant\begin{matrix}[CH\cdot OH]_3\cdot CO\cdot NH\cdot NH \\ N\cdot NH\cdot C_6H_4\cdot NH-NH\end{matrix}\!\!>C_6H_4.$$

It dissolves comparatively easily in the ordinary solvents, and also in solutions of acids and alkalis. Fehling's solution and ammoniacal silver solutions are reduced by it in the cold. If its alcoholic solution is heated with ferric chloride and the cooled liquid shaken with chloroform, the latter assumes an intense blood-red coloration, whilst the aqueous alcoholic layer becomes pale green. T. H. P.

5-Azoeugenol and its Constitution. GIUSEPPE ODDO and ERNESTO PUXEDDU (*Gazzetta*, 1905, **35**, i, 55—73).—When an alkaline solution of eugenol (1 mol.) is treated in the cold with the solution of a diazonium salt (1 mol.), precipitation of azoeugenol takes place immediately. The benzeneazo-, *m*-bromobenzeneazo-, and *β*-naphthalene-azo-compounds of eugenol, described in the present paper, behave towards alkalis like azophenols, and towards acetic anhydride like hydrazones of quinone, so that either of these constitutions may be ascribed to them.

Benzeneazoeugenol, $\begin{matrix}OH\cdot C\cdot C(OMe)\colon CH \\ N_2Ph\cdot C-CH=C\cdot C_3H_5\end{matrix}$, prepared by the addition of the diazo-solution obtained by the action of sodium nitrite on aniline (1 mol.) to an aqueous solution of eugenol (1 mol.) containing sodium hydroxide (2 mols.), crystallises from aqueous alcohol in long, dark red, silky needles, which melt at 75—76° (compare Borsche and Streitberger, Abstr., 1904, i, 1064) and have the normal molecular weight in freezing benzene; it dissolves in dilute alkali solutions, giving an intense red coloration, reacts energetically with concentrated nitric acid, but is not dissolved by hydrochloric acid, although tin and hydrochloric acid or zinc and acetic acid convert it into aniline and aminoeugenol; it dissolves readily in alcohol, benzene, chloroform, acetone, or acetic acid, and to a less extent in ether or light petroleum; when crystallised from very dilute alcohol, it is obtained in yellow leaflets which melt at 79—80° and are probably hydrated, since an hour's heating at 60° converts them into the red needles melting at 75—76°. With bromine in chloroform solution, it yields the *dibromide*, $C_{16}H_{16}O_2N_2Br_2$, which crystallises from a mixture of light petroleum and benzene, or from alcohol in golden-yellow scales melting at 98°. The *ethyl* derivative, $C_{18}H_{20}O_2N_2$, forms a dark red, oily liquid boiling at 175° under 30 mm. pressure; it is soluble in dilute alkali solutions, and hence does not possess the character of an oxygen-ether. Benzeneazoeugenol does not undergo hydrolytic dissociation when boiled with hydrochloric acid or when its alcoholic solution is boiled with alkali hydroxide. It does not react with phenylhydrazine or hydroxylamine, but combines with 1 mol. of hydrogen chloride forming an unstable *hydrochloride*, which is obtained in long, white crystals melting at about 75°. The *acetyl* derivative, $C_{18}H_{18}O_3N_2$, separates from light

petroleum in orange-red, acicular crystals, melts at 65°, and dissolves readily in alcohol, ether, benzene, or chloroform; when boiled with alcoholic hydrogen chloride, it is converted into benzeneazoeugenol, whilst zinc and acetic acid transform it into acetanilide and aminoeugenol, so that the acetyl group must be united to nitrogen, thus: $NPhAc\cdot N:C<{CH:C(C_3H_5) \atop CO\cdot C(OMe)}>CH$.

m-*Bromobenzeneazoeugenol*, $C_6H_4Br\cdot N_2\cdot C<{C(OH)\cdot C(OMe) \atop CH = C(C_3H_5)}>CH$, prepared in similar manner to benzeneazoeugenol, separates from light petroleum as a dark red, crystalline powder melting at 100°, and is moderately soluble in all the common organic solvents; its colour is somewhat intensified by dilute alkali hydroxide solution, and after boiling with sodium ethoxide in alcoholic solution the addition of water precipitates a voluminous, yellow compound melting at 96°; it is soluble in concentrated sulphuric acid with formation of a dark red coloration, and reacts with fuming nitric acid so energetically that it ignites; it does not react with phenylhydrazine or hydroxylamine; the *acetyl* derivative, $C_{18}H_{17}O_3N_2Br$, separates from alcohol in orange-coloured, prismatic needles melting at 92—93° and soluble in the more common organic solvents, and is converted into *m*-bromobenzeneazoeugenol and ethyl acetate by boiling its alcoholic solution with hydrochloric acid.

β-Naphthaleneazoeugenol, $C_{10}H_7\cdot N_2\cdot C<{C(OH)\cdot C(OMe) \atop CH = C(C_3H_5)}>CH$, crystallises from alcohol in small, nearly black, prismatic needles, which give a brick-red powder, melts at 102°, and is soluble in the more common organic solvents; it dissolves in concentrated sulphuric acid, giving a reddish-brown coloration, and reacts energetically with fuming nitric acid; it does not react with phenylhydrazine or hydroxylamine, but yields an unstable, crystalline *hydrochloride*, and, on reduction with tin and hydrochloric acid, gives aminoeugenol; the *sodium* derivative, $C_{20}H_{17}O_2N_2Na$, forms an intense carmine-red, crystalline precipitate, melting and decomposing at 233°, and is reconverted into *β*-naphthaleneazoeugenol by dilute hydrochloric acid; the *acetyl* derivative, $C_{10}H_7\cdot NAc\cdot N:C<{CH:C(C_3H_5) \atop CO-C(OMe)}>CH$, crystallises from alcohol in red needles melting at 108° and soluble in benzene or light petroleum, and, on reduction with zinc and acetic acid, yields aceto-*β*-naphthalide and aminoeugenol. T. H. P.

Action of Diazonium Compounds on Malonic Acid. Max Busch and Wilh. Wolbring (*J. pr. Chem.*, 1905, [ii], 71, 366—381. Compare Abstr., 1903, i, 537).—*o*-Nitrophenyldiazonium acetate reacts with malonic acid, yielding di-*o*-nitroformazyl and the *o*-nitrophenylhydrazone of glyoxylic acid.

Di-o-nitroformazyl, $NO_2\cdot C_6H_4\cdot N_2\cdot CH:N\cdot NH\cdot C_6H_4\cdot NO_2$, crystallises in dark red needles and melts at 186—187°. The *ammonium* salt, $(NO_2\cdot C_6H_4\cdot NH\cdot N:CH\cdot CO_2H)_2NH_3$, crystallises in orange needles and melts and decomposes at 197—198°. The *silver* salt, $C_8H_6O_4N_3Ag$, crystallises in grey needles; the *sodium* salt forms needles; the

methyl ester crystallises in yellow, glistening needles and melts at 140°; the *ethyl* ester forms yellow needles and melts at 106°.

p-Nitrophenyldiazonium acetate reacts with malonic acid, forming di-*p*-nitroformazyl, as a brown, crystalline powder, and the p-*nitrophenylhydrazone* of glyoxylic acid. The *ammonium* salt, $C_{16}H_{17}O_8N_7$, forms a yellow, crystalline mass, which commences to sinter at 190° and melts and decomposes at 250°.

The action of *m*-nitrophenyldiazonium acetate on malonic acid leads to the formation of the formazyl compound only.

o-Bromophenyldiazonium acetate reacts with malonic acid to form the o-*bromophenylhydrazone* of glyoxylic acid, which crystallises in yellow needles and melts at 156°. *p*-Bromophenyldiazonium acetate and malonic acid yield *di*-p-*bromoformazyl*, which forms dark red, crystalline aggregates and melts at 114—115°.

The o-*iodophenylhydrazone* of glyoxylic acid crystallises in glistening, yellow leaflets and melts and decomposes at 160°. *Di*-o-*iodoformazyl* crystallises in glistening, red needles and melts and decomposes at 168—169°.

The action of *o*-chlorophenyldiazonium acetate and sodium nitrite on malonic acid leads to the formation of o-*chlorophenylazoformaldoxime*, $C_6H_4Cl{\cdot}N{:}N{\cdot}CH{:}N{\cdot}OH$, which crystallises in glistening, orange needles, melts at 150°, and is reduced by zinc dust or ammonium sulphide in alcoholic solution to o-*chlorophenylhydrazoformaldoxime*; this crystallises in glistening, white leaflets, becomes red at 133°, melts and decomposes at 137°, and is easily oxidised to the azo-compound. When warmed with concentrated hydrochloric acid, *o*-chlorophenylazoformaldoxime gradually dissolves, and the solution deposits ω-p-*dichlorophenylhydrazoformaldoxime* in colourless needles melting at 143°.

α-*Naphthylazoformaldoxime* crystallises in yellow, microscopic needles, or glistening, dark red needles, and melts and decomposes at 151—152°. β-*Naphthylazoformaldoxime* crystallises in small, yellow or long, red needles and melts at 155—156°. Phenylazoformaldoxime is formed by the action of phenyldiazonium acetate and sodium nitrite on malonic acid (compare Bamberger and Frei, Abstr., 1902, i, 404). o-*Tolylazoformaldoxime* is a reddish-yellow oil. o-*Anisylazoformaldoxime* crystallises in yellow needles and melts at 140—141°. as-m-*Xylylazoformaldoxime*, from *as-m*-xylyldiazonium acetate, malonic acid, and sodium nitrite, crystallises in slender, yellow needles and melts at 125°. G. Y.

Action of Diazonium Compounds on Iminazoles. Hermann Pauly (*Zeit. physiol. Chem.*, 1905, **44**, 159, 160).—Polemical. A reply to Burian (*ibid.*, **43**, 502). J. J. S.

Secondary Diazoamino-compounds. Léo Vignon and Adolphe Simonet (*Compt. rend.*, 1905, **140**, 1038—1040. Compare this vol., i, 397).—Methylanilinoazobenzene, $NPh{:}N{\cdot}NMePh$, is obtained by adding an aqueous solution of diazobenzene chloride to an alcoholic solution of methylaniline, and separates in the form of a yellow oil on

adding excess of water. By the same method several other secondary diazoamino-compounds were obtained.

Ethylanilinoazobenzene, NPh:N·NEtPh, forms an orange-yellow oil which partially solidifies after being kept for some time.

Benzylanilinoazobenzene, NPh:N·NPh·CH_2Ph, separates as a red oil which solidifies and melts at 74°.

Dibenzylaminoazobenzene, NPh:N·N(CH_2Ph)$_2$, crystallises in pale yellow needles melting at 83°.

Diethylaminoazobenzene, NPh:N·NEt_2, separates in the form of a mobile, red liquid and boils at 258—260°.

Acids hydrolyse these diazoamino-compounds, yielding nitrogen, phenol, and the secondary amines. H. M. D.

Adsorption Theory of the Neutralisation of Toxins and Related Phenomena. WILHELM BILTZ, H. MUCH, and C. SIEBERT (*Chem. Centr.*, 1905, i, 1107—1108; from *Behring's Beitr. exper. Therapie*, Heft 10).—The experiments indicate that all + colloids precipitate proteid solutions of various kinds; in general, − colloids do not bring about precipitation. The action of the various colloids on solutions of saponin leads to the same subdivision. Solutions of many specific proteid materials become less active when shaken up with various hydrogels. The hydroxide hydrogels have approximately the same effect on a given solution. If the concentration of the proteid is varied, the effect produced by a given quantity of hydrogel is relatively greater in the dilute solutions.

The diminution of the activity of the proteid solution cannot be explained on the assumption that the proteid is simply absorbed unchanged by the hydrogel, for unchanged active substance cannot be extracted from hydrogels which have been shaken up with proteid solutions. The effect of the colloids is rather to increase the rate of decomposition of the proteids. The authors regard the action as a "neutralisation phenomenon," which takes place in two stages. In the first, absorption of the active substance by the colloid takes place, and in the second the absorbed substance decomposes. The diminution of the activity of the solution is thus determined by the individual velocities of these consecutive changes. H. M. D.

Separation of Proteids. H. C. HASLAM (*J. Physiol.*, 1905, 32, 267—290).—Attention is drawn to the inexactitude of various methods for the separation of proteids by precipitation, especially by neutral salts. The precipitate should be redissolved and again precipitated, and this repeated until the organic nitrogen in the filtrate is constant. When the proteid it is sought to purify is in the filtrate, other proteids being got rid of by precipitation, the treatment is more complicated, and a method of fractional precipitation, to be carefully distinguished from Pick's method of taking fractions, is described at length. The previous methods in use are quite inadequate to obtain pure substances. By the new methods it is shown that albumoses can be separated from peptones, and that there are three primary albumoses (hetero-, α-proto-, and β-proto-). Among other practical points, the

use of sodium sulphate at 37° is recommended instead of ammonium sulphate; the estimation of nitrogen in the filtrate is then simpler.

It is stated that, in the usual fractional method, each fraction contains every proteid in a mixture; the first fractions will naturally contain a large quantity of the most insoluble and a small quantity of the most soluble; the last fractions the reverse. The doctrine of natural boundaries in salting out leads to erroneous results. It is suggested that some sort of loose chemical combination existing between the proteids in a mixture will explain the tenacity with which they cling together.

W. D. H.

The Carbohydrate Group in Proteids. LEO LANGSTEIN (*Beitr. chem. Physiol. Path.*, 1905, **6**, 349—357. Compare Abstr., 1903, i, 734).—The researches of previous workers on this question show great differences of opinion as to the character and amount of the carbohydrate group in proteids, some even denying that it exists at all in certain proteids. Among these investigations, the discovery of glucoalbumoses by Pick and Umber among the digestive products of egg-albumin is regarded as important. In the present research, the carbohydrate group in serum-albumin was found not in an albumose, but as a gluco-peptone in the ammonium sulphate filtrate. In regard to the globulin, the proteolytic experiments confirm the previous conclusion that several carbohydrates are obtainable, and that the carbohydrate group or groups are chemically combined with the original proteid, and not merely mechanically mixed. The fact that the blood proteids have such a composition is an important factor in the explanation of diabetes.

W. D. H.

Proteid Chemistry. EMIL ABDERHALDEN (*Chem. Centr.*, 1905, i, 884; from *Med. Klin.*, 1905, **1**, Nos. 1 and 2).—The following simple products have been as yet obtained on hydrolysing proteids: glycine, alanine, aminovaleric acid, leucine, *iso*leucine, phenylalanine, glutamic acid, aspartic acid, cysteine, α-proline (pyrrolidine-2-carboxylic acid), hydroxy-α-proline, serine, tyrosine, tryptophan, lysine, arginine, histidine, diaminotrihydroxydodecoic, diaminoglutaric, diaminoadipic, aminohydroxysuccinic, and diaminosuberic acids, an acid $C_9H_{16}O_7N_2$ (caseic acid), and an acid $C_{12}H_{24}O_5N_2$ (caseic acid).

The similarity of Fischer's synthetical polypeptides with the natural peptones is pointed out, and stress is laid on the importance of the action of the pancreas fragments on these polypeptides as throwing light on the different forms of linking of the amino-acids in the proteid molecule.

E. F. A.

Physical Alterations of Colloids. IV. Precipitation of Albumin by means of Salts of Heavy Metals. WOLFGANG PAULI (*Beitr. chem. Physiol. Path.*, 1905, **6**, 233—259. Compare Abstr., 1902, ii, 388; 1903, i, 299; 1904, i, 356; Galeotti, *ibid.*, 1904, i, 355).—The precipitating action of solutions of the following salts of heavy metals on albumin solutions has been studied: cupric sulphate, cupric acetate, ferric chloride, ferric nitrate, zinc acetate, zinc chloride, lead acetate, silver nitrate, and mercuric chloride.

With zinc sulphate solutions, the precipitating action increases with the concentration of the sulphate from $0{\cdot}001N$ to $0{\cdot}05N$ for 20 per cent. albumin, then decreases, and finally disappears at a concentration between 1 and $2N$, but reappears again at higher concentrations. The precipitations with the more dilute solutions are non-reversible, whereas those with the concentrated solutions are reversible. With more concentrated albumin solutions, the precipitation is more copious, and the interval between non-reversible and reversible precipitation is smaller.

The phenomena of double precipitation maximum and difference of reversibility of the two maxima have not been observed with other readily soluble salts.

For a 10 per cent. albumin solution, the lowest concentration of cupric sulphate which produces precipitation is about $0{\cdot}0008$—$0{\cdot}001N$, but a normal solution does not produce precipitates nor even a $6N$ solution. With excess of albumin, the process is somewhat different (compare Galeotti, *loc. cit.*).

Silver nitrate represents a third type, and its precipitating action on 10 per cent. albumin is much the same with solutions varying from $0{\cdot}1$—$6N$.

With horse serum diluted 100 times, and dialysed until its conductivity had fallen to that of distilled water, silver nitrate solutions varying from $0{\cdot}1$ to $2{\cdot}0N$ gave no indication of a maximum, and also no signs of resolution of the precipitate.

The influence of salts of the alkali metals on the precipitating power of dilute ($0{\cdot}005N$) solutions of zinc sulphate has been studied. All have an inhibiting influence, and this increases in the order SO_4'', Cl', $C_2H_3O_2'$, NO_3', Br', I', SCN' for anions and $K^{\cdot}$, $Na^{\cdot}$, $NH_4^{\cdot}$, $Mg^{\cdot\cdot}$ for cations. With more concentrated zinc solutions ($4N$), the alkali salts have an intensifying action in the same order as given above for the anions. The phenomena observed here are very similar to those previously obtained by the addition of alkali salts to the alkali earth salts. The paper concludes with a chapter on the theory of albumin precipitation. J. J. S.

Oxidation of Albumins. OTTO VON FÜRTH (*Beitr. chem. Physiol. Path.*, 1905, **6**, 296—328. Compare Maly, Abstr., 1885, 824; 1889, 629; Löw, *ibid.*, 1885, 823; Bondzyński, *ibid.*, 1894, i, 479; Würster, *ibid.*, 1887, 607; Schulz, *ibid.*, 1900, i, 266; Bernert, *ibid.*, 1899, i, 315). —Maly's peroxyprotoic acid, obtained by oxidising casein with potassium permanganate in alkaline solution, is a mixture of at least three compounds of high molecular weight. These may be separated by fractional precipitation with silver nitrate, lead acetate, and mercuric acetate, and are termed A, B, and C peroxyprotoic acids. The compounds A and C do not differ materially from Maly's acid, whereas B contains much more oxygen and much less nitrogen.

The acids may readily be esterified by means of alcohol and hydrogen chloride. The *esters* are readily soluble in absolute alcohol or chloroform and are precipitated by the addition of ether to their chloroform solutions. They are hydrolysed by aqueous ammonia and appear to yield the unaltered acids. When boiled for several hours

with baryta water, the peroxyprotoic acids yield considerable quantities of barium oxalate and ammonia together with *diaminoprotoic acids.* These are biuret compounds which yield glutamic acid, benzoic acid, leucine, and ammonia on hydrolysis. Unlike the original peroxyprotoic acids, these diaminoprotoic acids are readily oxidised by alkaline permanganate at the ordinary temperature, yielding amorphous biuret derivatives—*Kyroprotoic acids*—which, on hydrolysis, yield leucine, glutamic acid, oxalic acid, and ammonia.

The mean composition of the various compounds is :

	C.	H.	N.	O.	
Casein	53·0	7·0	15·7	22·65	per cent.
Maly's oxyprotosulphonic acid	51·21	6·89	14·59	25·54	,,
Peroxyprotoic acid A and B	45·74	6·08	13·97	33·06	,,
Kyroprotoic acid A	43·24	6·42	11·08	38·68	,,
Peroxyprotoic acid B	42·33	5·88	8·96	41·80	,,

J. J. S.

Specific Rotation of Salts of Casein. John H. Long (*J. Amer. Chem. Soc.*, 1905, **27**, 363—366).—The following determinations were made at 20°. A solution made by dissolving 5 grams of casein in 45 c.c. of $N/10$ sodium hydroxide and diluting the product with water to 100 c.c. is neutral to phenolphthalein, and gives $[\alpha]_D - 103·5°$ (based on the weight of casein). When only half this quantity of alkali is employed, $[\alpha]_D = -95·2°$. A solution containing 5 grams of casein in 45 c.c. of $N/10$ potassium hydroxide, diluted with water to 100 c.c., gives $[\alpha]_D - 104·4°$. A similar solution of casein in lithium hydroxide solution gives $[\alpha]_D - 100·8°$, whilst a solution containing only 22·5 c.c. of $N/10$ lithium hydroxide gives $[\alpha]_D - 94·8°$. The ammonium salt, made by dissolving 5 grams of casein in 45 c.c. of $N/10$ ammonia and diluting to 100 c.c., gives $[\alpha]_D - 97·8°$. In all these cases, the value of $[\alpha]_D$ is increased by increasing the amount of alkali.

Béchamp (Abstr., 1891, 339) has shown that casein is slightly soluble in water, and with such a solution he found $[\alpha]_D - 105°$, which is practically the same as the value found for the salts. The specific rotatory power is therefore a constant, and may be utilised in comparing milks from different sources. E. G.

Casein and Paracasein in some of their Relations to Bases and Acids. Lucius L. van Slyke and Edwin B. Hart (*Amer. Chem. J.*, 1905, **33**, 461—496. Compare Abstr., 1903, i, 215).—The existence of two calcium compounds of casein, one of which contains about 2·40 per cent. and the other about 1·50 per cent. of calcium oxide (Söldner, Abstr., 1889, 634), has been confirmed. The former of these salts is termed basic calcium casein, and the latter normal calcium casein. Neither of these calcium compounds is coagulated by rennet enzyme alone, but the normal calcium casein is coagulated by rennet in presence of soluble calcium salts. Both compounds are coagulated if heated to 35—45° with a soluble calcium salt, such as calcium chloride. The normal calcium casein behaves in these respects just

like milk-casein, and it is probable that the casein of cow's milk exists in the form of this compound.

The base-free casein, prepared directly from milk or by treating a solution of casein in calcium hydroxide with acid until it is acid to litmus, is readily soluble in 5 per cent. sodium chloride or in hot 50 per cent. alcohol. This substance was formerly regarded as a casein mono-salt (or unsaturated salt) of the acid used in its precipitation. On treating free casein with dilute acids, salts are formed which correspond with the compounds previously termed di-salts (or saturated salts).

Paracasein closely resembles casein in its chemical properties and yields two calcium salts containing 2·40 and 1·50 per cent. of calcium oxide respectively, but whilst the normal calcium salt of casein is not coagulated by soluble calcium salts, except on warming to 35—45°, that of paracasein is readily coagulated at the ordinary temperature. It is therefore probable that paracasein only differs from casein in consisting of larger molecular aggregates. Free paracasein appears to be identical with the substance which was formerly regarded as a mono-salt of the acid used in its preparation, whilst its compounds with acids are apparently the substances previously termed di-salts. Thus the substance which is extracted from cheese by means of salt solution or hot alcohol, and was previously regarded as paracasein monolactate, has now been found to consist of free paracasein.

When an acid is formed in, or added to, milk, it unites with the calcium combined with the casein and the free casein is precipitated. On further addition of acid, the casein combines with it to form a casein salt; in the case of lactic acid, the substance so formed is the ordinary coagulum which is produced when milk turns sour. The coagulum formed by the action of rennet enzyme on milk is calcium paracasein, either mixed or loosely combined with soluble calcium salts. In the manufacture of cheddar cheese, the lactic acid produced reacts with the calcium paracasein with formation of free paracasein and calcium lactate.

The following nomenclature is suggested. The compound existing in cow's milk is called calcium casein, the term casein being reserved for the free proteid. The substance containing 2·40 per cent. of calcium oxide is termed basic calcium casein, and the compounds formed by the union of the proteid with acids are called casein salts of the acids. A similar nomenclature is applied to paracasein and its compounds; the term calcium paracasein, however, is reserved for the uncoagulated form, whilst the coagulated form is referred to as coagulated calcium paracasein. E. G.

Presence of Fibrinoglobulin in Fibrinogen Solutions. WILLEM HUISKAMP (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, **13**, 610—612; *Zeit. physiol. Chem.*, 1905, **44**, 182—197).—Calugareanu (*Arch. intern. Physiol.*, **2**, 12) states that the addition of sodium fluoride to the extent of 3 per cent. to plasma produces fibrin formation. What really occurs, however, is a precipitate of fibrinogen; in oxalate plasma this is gelatinous, in ox or rabbit's plasma it is flocculent. It may be redissolved and made to clot, that is, it is

converted into fibrin by means of fibrin ferment. The liquid residue then contains no fibrinoglobulin. Sodium fluoride is a good precipitant for fibrinogen, and leaves the fibrinoglobulin in solution when it is present, as in plasma or fibrinogen solutions as prepared by the ordinary method. Hammarsten believes that under the influence of fibrin ferment or of heat, the fibrinogen molecule is split into fibrin and fibrinoglobulin, or else that fibrinoglobulin is a changed soluble fibrin. The latter proteid, however, is not formed in this way. It is present before clotting takes places. W. D. H.

Spectroscopy of Oxyhæmoglobin. M. Piettre and A. Vila (*Compt. rend.*, 1905, **140**, 1060—1062).—Oxyhæmoglobin, when crystallised, is not to be regarded as the same thing as the pigment of the red corpuscles during life. The principal ground on which this conclusion is reached is that solution of the crystals shows a third absorption band with its centre at $\lambda = 634$. Desiccation, exposure of the crystals to the air, and numerous reagents increase the intensity of this band. By treatment with small quantities of sodium fluoride, its centre shifts to $\lambda = 612$. This may even be used for the detection of quite small amounts of fluoride. W. D. H.

A Fluorine Combination of Methæmoglobin. J. Ville and E. Derrien (*Compt. rend.*, 1905, **140**, 1195—1197. Compare this vol., i, 399).—The change produced by the addition of sodium fluoride or hydrofluoric acid to methæmoglobin led to a search for a fluorine compound of this pigment. This was obtained in the form of crystals, which, however, rapidly decompose with the formation of methæmoglobin.

The spectrum of the fluorine preparation is characterised by two absorption bands, of which the centre of the first is at $\lambda = 612$, and of the second at $\lambda = 494$. The two middle bands have disappeared. The spectrum of oxyhæmoglobin is not modified by sodium fluoride. No reference is made to the work of Piettre and Vila (see preceding abstract). W. D. H.

Identity of Phylloerythrin, Bilipurpurin, and Cholehæmatin. Leon Marchlewski (*Bull. Acad. Sci. Cracow*, 1904, 505—508).—The substance prepared from herbivorous bile by Loebisch and Fischler and named by them bilipurpurin is the same material previously named cholehæmatin by MacMunn. Gamgee suggested that cholehæmatin is identical with phylloerythrin; this, mainly on spectroscopic grounds, is shown to be correct. W. D. H.

Organic Chemistry.

Catalytic Action of Finely Divided Metals. A. Mailhe (*Chem. Zeit.*, 1905, **29**, 462).—This is a summary of the work done by Sabatier and Senderens, the author, and others on the catalytic action of finely divided iron, nickel cobalt, and copper (compare this vol., i, 401, and references therein given).

Sabatier and Senderens have quite recently converted aliphatic nitriles into amines by passing them over nickel at 180° in presence of hydrogen; benzonitrile under this treatment, however, gives toluene and ammonia, but not benzylamine. P. H.

Changes effected by Time on Hydrocarbon Substances of Organic Origin. Marcellin Berthelot (*Ann. Chim. Phys.*, 1905, [viii], **5**, 165—174).—A *résumé* of work already published (compare Abstr., 1900, i, 3; this vol., i, 169). M. A. W.

Physical Properties of Propane. Paul Lebeau (*Compt. rend.*, 1905, **140**, 1454—1456).—Propane, prepared from *n*-propyl iodide or from *iso*propyl iodide or chloride (compare this vol., i, 401), boils at $-44·5°$ under 757 mm. pressure, has a critical temperature 97·5°, and critical pressure 45 atmos. These results are in close agreement with the values already found by Olszewski (compare *Bull. Acad. Sci. Cracow*, 1889). Both propane and ethane are liquid at $-195°$, and in this respect differ from methane, which solidifies at $-184°$ (compare Olszewski, Abstr., 1885, 860, and Moissan and Chavanne, this vol., i, 253). The solubility of propane in various solvents has been determined, and the results are comprised in the following table:

	Pressure in millimetres of mercury.	Temperature.	Volumes of gas dissolved in 10 vols. of solvent.
Water	753	17·8°	0·65
Alcohol	754	16·6	790
Ether	757	16·6	926
Chloroform	,,	21·6	1299
Benzene	,,	21·5	1452
Turpentine	,,	17·7	1587

M. A. W.

Preparation of Methyl Bromide. Wilhelm Steinkopf and Wilhelm Frommel (*Ber.*, 1905, **38**, 1865—1868).—An apparatus is figured for the preparation of methyl bromide by the action of bromine on a mixture of methyl alcohol and red phosphorus. The product is passed through water and aqueous sodium hydroxide, then over potassium hydroxide and calcium chloride, cooled in a condenser surrounded by a freezing mixture, and collected in a receiver cooled by solid

carbon dioxide. Methyl bromide is a mobile liquid at $-84°$, solidifies to a white, crystalline mass when cooled by liquid air, and boils at $4·5°$ under 758 mm. pressure. To observe the correct boiling point, it is necessary to surround the distillation apparatus completely with water at $6°$, otherwise too high a boiling point is observed (compare Bunsen, *Annalen*, 1843, **46**, 44; Pierre, *Ann. Chim. Phys.*, 1845, [iii], **15**, 373; Pierre and Puchot, *Compt. rend.*, 1872, **75**, 1442). G. Y.

Action of Metal-ammonium Compounds on Halogen Derivatives of Methane. E. CHABLAY (*Compt. rend.*, 1905, **140**, 1262—1263).—When methyl chloride is passed into a solution of sodammonium, sodium chloride, methane, methylamine, and ammonia are produced according to the equation $2NH_3Na + 2CH_3Cl = 2NaCl + CH_4 + NH_2·CH_3 + NH_3$.

Chloroform reacts with sodammonium, but the change is of a complex character; sodium chloride, sodamide, and sodium cyanide are formed as solid products, and methane mixed with small quantities of ethylene and acetylene is evolved.

Iodoform dissolves in liquid ammonia, and on cooling to $-78°$ the solution deposits white crystals of the composition CHI_3,NH_3. The vapour pressure of the crystals is equal to 760 mm. at $-14°$.

Sodammonium reacts readily with the ammoniacal solution of iodoform; sodium iodide and cyanide separate, and methane mixed with small quantities of ethylene, acetylene, hydrogen, and nitrogen is evolved. The reaction between sodammonium and carbon tetrachloride is similar, the products formed being sodium chloride, sodium cyanide, methane, and a little nitrogen. H. M. D.

Action of Metal-ammonium Compounds on Alcohols. General Method for the Preparation of Alkyloxides. E. CHABLAY (*Compt. rend.*, 1905, **140**, 1343—1344).—The alkali metal is dissolved with special precautions, which are described in the original, in liquid ammonia and the solution is added gradually to the required alcohol in the case of primary alcohols and *vice versâ* in the case of secondary or tertiary alcohols. With primary alcohols, action progresses rapidly, and a precipitate of the alkyloxide is formed. With secondary and tertiary alcohols, the action is slow and is masked to some extent by a secondary reaction represented by the equation $2NH_3Na = 2NH_2Na + H_2$. The alkyloxides of the *sec.*- and *tert.*-alcohols are soluble in liquid ammonia and can only be isolated, combined with alcohol, by evaporation of the solvent. The *sodium* derivative of trimethylcarbinol crystallises in needles containing an uncertain amount of the alcohol, which can be driven off by heating the crystals, when the alcohol-free sodium derivative is left in the form of a white powder. T. A. H.

Action of Metal-ammonium Compounds on Polyatomic Alcohols. E. CHABLAY (*Compt. rend.*, 1905, **140**, 1396—1398).—The alkali metal-ammonium compounds react with the polyatomic alcohols in the cold, and monosubstituted alkali derivatives are formed with evolution of hydrogen.

Mannitol, erythritol, glycol, and glycerol were used in the experi-

ments, and the quantities of hydrogen evolved were measured. Mannitol dissolves readily in liquid ammonia, and on evaporation crystals of the composition $C_6H_{14}O_6,NH_3$ are obtained. The dissociation tension of these is 520 mm. at 0° and 760 mm. at 14°. When excess of mannitol is added to a solution of sodammonium, the blue colour of the latter quickly disappears and the monosodium compound of mannose separates out. It is readily purified by washing with liquid ammonia, which removes the excess of mannitol. Since sodammonium slowly decomposes with the formation of sodamide, which is insoluble in liquid ammonia, it is preferable to use potassammonium when a pure product is required, potassamide being readily soluble. On evaporation of a solution of erythritol in liquid ammonia, well formed crystals of the composition $C_4H_{10}O_4,4NH_3$ remain behind. The monopotassium derivative of erythritol was isolated in the same manner as the mannitol compound.

The same method leads to the formation of alkali derivatives of menthol and borneol. H. M. D.

The Acidity of Commercial Ethyl Alcohol and its Variations at the Ordinary Temperature. René Duchemin and Jacques Dourlen (*Compt. rend.*, 1905, **140**, 1466—1468).—Commercial ethyl alcohol commonly contains acetic acid due to the oxidising action of the air on the alcohol; the quantity of acid varies with the time of exposure to the air, and also with the nature of the vessel in which the alcohol is kept, the increase being greater in the case of green glass vessels than white glass; this is due either to the catalytic action of the former (compare Trillat, Abstr., 1903, i, 222) or to the fact that the alkali it contains is not so readily available for neutralising the acid as is the case with white glass, thus, an alcohol which contained initially 0·014 gram of acetic acid per litre showed the following changes in acidity after 34 days: +0·0024 in green glass −0·0036 in white glass; +0·0036 in tinned iron; and −0·0024 in copper. After bubbling 72 litres of air through an alcohol exactly neutralised by sodium hydroxide, the acetic acid formed amounted to 0·014 gram per litre. M. A. W.

Action of Alkalis on Aqueous Solutions of Acetol. André Kling (*Compt. rend.*, 1905, **140**, 1256—1259).—Acetol in aqueous solution behaves as a pseudo-acid (or aci-compound, compare Hantzsch, this vol., i, 317) in that it is only gradually neutralised by an alkali and is more acid towards the pseudo-acid indicators, phenolphthalein or litmus, than towards methyl-orange, thus, 1 mol. of acetol is neutralised by 0·01 mol. KOH in the presence of methyl-orange, but requires 0·09 mol. KOH when phenolphthalein or litmus is used as indicator. Experiments on the electrical conductivity of aqueous alkaline solutions of acetol show that the resistance of the solutions increases with the time up to a certain limit, when it becomes constant, and this is characteristic of pseudo-acids. M. A. W.

Propionylcarbinol and its Derivatives. André Kling (*Compt. rend.*, 1905, **140**, 1345—1347. Compare this vol., i, 172, 327, and preceding abstract).—Propionylcarbinol $OH{\cdot}CH_2{\cdot}COEt$ (ketonic

form) or $O<\begin{matrix}CEt\cdot OH\\ |\\ CH_2\end{matrix}$, (aci- or pseudo-acid form), boils at 79—80° under 30 mm. or at 153—154° under 760 mm. pressure, has a sp. gr. 1·0365 at 15°/15° and n_D = 1·4315 at 14·5°, whence the mol. refraction is 21·998 (the ketonic form requires 22·216 and the aci-form 21·612). It reduces Fehling's solution and may be estimated in this way, 1 gram being equivalent to 1·36 gram of copper in the form of cuprous oxide. Cupric hydroxide oxidises it to α-hydroxybutyric acid and sodium or aluminium amalgam reduces it, forming a mixture of butanone, α-butanol and butane-αβ-diol; the latter boils at 192—194°.

Propionylcarbinol yields an *oxime* melting at 60—61° and furnishes a crystalline additive *product* with sodium hydrogen sulphite. With semicarbazide, two condensation products are formed. The first, obtained when the action takes place in water, melts at 66° and may have the constitution $\begin{matrix}O—\\ |\\ CH_2\end{matrix}>CEt\cdot NH\cdot NH\cdot CO\cdot NH_2$, and the second, produced when the two substances react in alcohol, melts at 135—136° and is probably a true semicarbazone.

Propionylcarbinyl formate, obtained by the action of potassium formate on the chloro-derivative of the keto-alcohol, boils at 176—178°, has a sp. gr. 1·094 at 17°/17° and n_D 1·4245 at 17°, whence the mol. refraction is 27·070 (the ketonic form requires 27·008); the *semicarbazone* melts at 115°.

These observations indicate that propionylcarbinol, unlike acetol (mol. refraction 17·643, calculated for the ketonic form 17·614), normally exists in the two tautomeric forms and that the aci-form alone exists in aqueous solutions. The aci-form of propionylcarbinol is less active than that of acetol, since it does not react with methyl alcohol (*loc. cit.*). The esters exist only in the ketonic form. T. A. H.

Acetylmethylcarbinol (β-Hydroxy-γ-ketobutane). André Kling (*Compt. rend.*, 1905, **140**, 1456—1458. Compare Pechmann and Dahl, Abstr., 1890, 1234).—Acetylmethylcarbinol, prepared by the action of alcoholic potassium hydroxide on β-chloro-γ-ketobutane (compare Vladesco, Abstr., 1892, 810), polymerises in the presence of zinc to a crystalline solid which yields pure acetylmethylcarbinol on distillation, and a dextrorotatory isomeride (a_D = 2° for 1 dcm.) is obtained by the action of the sorbose bacteria or *Mycoderma aceti* on butan-βγ-diol. Acetylmethylcarbinol is a liquid with an agreeable odour, boils at 144—145°, has a sp. gr. 1·0108 at 15°/15° and n_D 1·4194 at 15°; it is oxidised to acetic acid by Fehling's solution and the reaction is quantitative; it forms a crystalline *semicarbazide* melting at 184—185°, sparingly soluble in water, a crystalline *compound* with sodium hydrogen sulphite soluble in water, and insoluble in ether, and is reduced by sodium or aluminium amalgam forming butanone, butan-β-ol and butan-βγ-diol. Like acetol and propionylcarbinol (compare Abstr., 1903, i, 138, 223; 1904, i, 2), acetylmethylcarbinol exists in aqueous solution in the oxidic form, $O<\begin{matrix}CMe\cdot OH\\ |\\ CHMe\end{matrix}$, tautomeric with the ketonic form, COMe·CHMe·OH, whilst the anhydrous compound is a

mixture of the two tautomeric forms having a molecular refraction 21·826 intermediate between the values 22·216 and 21·612 calculated for the ketonic and oxidic formulæ respectively. M. A. W.

α-Alkylhydracrylic Acids. EDMOND E. BLAISE and A. LUTTRINGER (*Bull. Soc. chim.*, 1905, [iii], **33**, 635—652. Compare Abstr., 1902, i, 357, 530, and this vol., i, 168).—Trioxymethylene, previously dried and finely powdered, is suspended in benzene, and to this is added one-third of the calculated quantity of ethyl α-bromobutyrate. To start the reaction, a small quantity of ethyl α-bromobutyrate is warmed in a test-tube with a zinc-copper couple, and the contents of the tube poured into the mixture. As the reaction slackens, further quantities of the bromo-ester are added. The first product of the reaction is probably the *zinc* compound, $ZnBr\cdot O\cdot CH_2\cdot CHEt\cdot CO_2Et$, which in contact with water furnishes ethyl α-ethylhydracrylate and zinc hydroxide and bromide. The secondary products, dipropyl ketone and ethyl β-hydroxy-αγ-diethylglutarate,

$$OH\cdot CH(CHEt\cdot CO_2Et)_2,$$

are formed during the condensation.

α-Ethylhydracrylic acid, $OH\cdot CH_2\cdot CHEt\cdot CO_2H$, prepared by hydrolysis of the crude ester obtained in the foregoing reaction, and purified by means of the *zinc calcium* salt, is a viscous liquid, which decomposes when heated even under a pressure of 0·1 mm. The *ethyl* ester boils at 96·5° under 13 mm. pressure and yields an *acetyl* derivative boiling at 95—96° under 11 mm. pressure; when the ethyl ester is prepared by esterification of the acid, the alcoholic hydroxyl of a portion of the ethyl ester undergoes esterification by a second mol. of the acid, forming a viscous, non-volatile liquid substance, which on heating decomposes into ethyl α-ethylacrylate and α-ethylhydracrylic acid. The *phenylhydrazide* of the acid $OH\cdot CH_2\cdot CHEt\cdot CO\cdot NH\cdot NHPh$ is crystalline, melts at 161°, and is slightly soluble in dry ether or benzene. The *phenylurethane*, prepared by the action of phenylcarbimide on the acid dissolved in alcohol, is crystalline, melts at 121°, and is readily soluble in water or ether, and slightly so in light petroleum.

α-Propylhydracrylic acid, $OH\cdot CH_2\cdot CHPr^{\alpha}\cdot CO_2H$, similarly prepared from ethyl α-bromovalerate, is a viscous liquid, slightly soluble in water; the *potassium* salt crystallises in brilliant lamellæ, and the *ethyl* ester boils at 117° under 18 mm. pressure. The *phenylhydrazide* of the acid, obtained by heating the phenylhydrazine salt at 110—120° during four hours, crystallises from warm alcohol and melts at 172°. The *phenylurethane* crystallises from boiling alcohol on addition of sufficient water to render the liquid turbid and melts at 116°.

α-iso*Propylhydracrylic acid*, $OH\cdot CH_2\cdot CHPr^{\beta}\cdot CO_2H$, obtained from ethyl α-bromo*iso*valerate, crystallises from dry ether and melts at 64°. The *ethyl* ester boils at 110° under 18 mm. pressure. The *phenylhydrazide* crystallises from boiling alcohol and melts at 192°, and the *phenylurethane* separates from benzene in crystals and melts at 133°.

α-Butylhydracrylic acid, obtained from ethyl bromohexoate by the general reaction and purified by means of the *benzylamine* salt (m. p. 80°), is a viscous liquid which does not solidify at −40°; its *ethyl* ester boils at 118—122° under 10 mm. pressure.

a-Heptylhydracrylic acid, prepared from *ethyl bromopelargonate* (a colourless liquid, boiling at 149—154° under 20 mm. pressure), crystallises from a mixture of ether and light petroleum and melts at 47—48°. The *potassium* salt forms brilliant lamellæ, and the *ethyl* ester boils at 165—166° under 22 mm. pressure. The *phenylurethane* crystallises from alcohol on addition of water and melts at 105°.

Ethyl β-hydroxy-αγ-diethylglutarate, $OH\cdot CH[CHEt\cdot CO_2Et]_2$, formed to a small extent during the condensation of trioxymethylene with ethyl α-bromobutyrate in presence of zinc or by a similar condensation with ethyl formate in place of trioxymethylene, boils at 149° under 10 mm. pressure. On hydrolysis with sodium hydroxide in aqueous solution, it yields the viscous free *acid,* which on treatment with acetyl chloride furnishes the *acetyl* derivative; this crystallises from alcohol on addition of water, melts and decomposes at 144°, yields an anilide melting at 144—145°, and when heated with a strong solution of sodium hydroxide yields β-hydroxy-αγ-diethylglutaric acid (m. p. 87°).

T. A. H.

Desmotropic Form of Substances of the Ethyl Acetoacetate Type in the Homogeneous State and Dissolved in Neutral Media. JULIUS W. BRÜHL and HEINRICH SCHROEDER (*Ber.*, 1905, **38**, 1868—1873. Compare this vol., i, 407).—An abstract of this paper appears in Proc., 1905, **21**, 164.

G. Y.

History of the Theory of the Formation and Constitution of Ethyl Sodioacetoacetate. ARTHUR MICHAEL (*Ber.*, 1905, **38**, 1922—1937).—A polemical paper in reply to Claisen (this vol., i, 258. Compare Michael, Abstr., 1901, i, 123). The formation of an additive compound, $ONa\cdot CMe(OEt)_2$, is considered improbable. The view that the acetoacetate formation and similar reactions are types of aldol condensations is further supported.

J. J. S.

Preparation of Ethyl Nitrosoacetoacetate. LOUIS BOUVEAULT and ANDRÉ WAHL (*Bull. Soc. chim.*, 1905, [iii], **33**, 559—561. Compare V. Meyer, Abstr., 1878, 396; Cérésole, Abstr., 1882, 1052; Wleugel, Abstr., 1882, 949; Jovitschitsch, Abstr., 1895, i, 447; 1896, i, 81; and Bouveault and Wahl, 1903, i, 677, and 1904, i, 556).—Ethyl acetoacetate, dissolved in alcohol, is mixed with a solution of sodium ethoxide in the same solvent, and a current of methyl nitrite is passed through the mixture. On removing the excess of alcohol by distillation, the sodium derivative of ethyl nitrosoacetoacetate is obtained, which is dissolved in water and the ester liberated by an acid and extracted with ether. Ethyl nitrosoacetoacetate, when freshly distilled, is a colourless, viscous liquid, which soon solidifies to a mass of crystals. It melts at 56°, boils at 155° under 15 mm. pressure, and gives an intense indigo-blue coloration in contact with metallic iron. In using Wolff's method for preparing this ester (Abstr., 1903, i, 203), the authors find it advisable to work at a temperature between −10° and 0°. No evidence of the existence of Jovitschitsch's stereoisomeric ester (*loc. cit.*) was obtained.

T. A. H.

Preparation of Ethyl Mesoxalate. RICHARD S. CURTISS (*Amer. Chem. J.*, 1905, **33**, 603—604).—Ethyl mesoxalate can be readily prepared by saturating ethyl malonate at $-15°$ with the nitrogen oxides obtained by the action of nitric acid on arsenious oxide. Several other substances are simultaneously produced and are at present under investigation. E. G.

New Synthesis of Oxalic Acid. HENRI MOISSAN (*Compt. rend.*, 1905, **140**, 1209—1211. Compare Abstr., 1903, ii, 365).—Dry carbon dioxide begins to react with potassium hydride at 54°, potassium formate being formed as the sole product. At 80°, the action is very energetic and a mixture of potassium formate and oxalate is produced, according to the equations $KH + CO_2 = KHCO_2$; $2KH + 2CO_2 = K_2C_2O_4 + H_2$. The quantities of formate, oxalate, and hydrogen were measured and the hydrogen found to correspond with the oxalate as required by the second equation. Sodium hydride reacts in a similar manner. H. M. D.

Unsymmetrical Compounds of the Malonic Series. FÉLIX MARGUERY (*Bull. Soc. chim.*, 1905, [iii], **33**, 541—548).—Ethyl hydrogen malonate, $CO_2H\cdot CH_2\cdot CO_2Et$, prepared by adding hydrochloric acid to a concentrated aqueous solution of the potassium salt (Massol, Abstr., 1891, 1012), is a colourless syrup, which boils at 147° under 21 mm. pressure, has a sp. gr. 1·1759 at 19°/19°, n_D 1·4275 at 19°, and when heated at 150° decomposes into ethyl acetate and ethyl malonate. *Ethyl hydrogen methylmalonate* boils at 144° under 18 mm. pressure, has a sp. gr. 1·1129 at 21°/21°, n_D 1·42455, is less soluble in water than the foregoing ester, and when heated under atmospheric pressure decomposes into ethyl propionate and carbon dioxide. *Ethyl hydrogen benzylmalonate* is a slightly yellow syrup, which decomposes when heated even under reduced pressure, has a sp. gr. 1·1477 at 19°/19°, n_D 1·51066, and when heated at 180° furnishes carbon dioxide and ethyl β-phenylpropionate, $CH_2Ph\cdot CH_2\cdot CO_2Et$. The *potassium* salts of these three esters are very hygroscopic.

The chloride of ethyl hydrogen malonate, prepared by the action of thionyl chloride on the ester, is a mobile, colourless liquid, boils at 68—70° under 13 mm. pressure, and when heated under the ordinary pressure decomposes at 170—180° into malonic acid and ethyl malonate (compare Blaise, Abstr., 1899, i, 331). The *chloride* of ethyl hydrogen methylmalonate boils at 100° under 45 mm. pressure and the corresponding *derivative* of ethyl malonic acid at 90—94° under 25 mm. pressure: the *chloride* of ethyl hydrogen benzylmalonate was not obtained pure. The *amide* of ethyl hydrogen methylmalonate, prepared by the action of dry ammonia on the chloride, crystallises in needles, melts at 68—69°, and is very soluble in ether, benzene, or boiling carbon disulphide. The amide of ethyl hydrogen ethylmalonate is similar and melts at 90°: that of ethyl hydrogen benzylmalonate melts at 92—93° (compare Bischoff and Siebert, Abstr., 1887, 951). T. A. H.

Ethyl Methylethyloxalacetate and some of its Derivatives. ARTUR MEBUS (*Monatsh.*, 1905, **26**, 483—495. Compare Wislicenus and Kieswetter, Abstr., 1898, i, 240).—*Ethyl methylethyloxalacetate*,

$CO_2Et \cdot CO \cdot CMeEt \cdot CO_2Et$, formed by boiling ethyl methyloxalacetate (Arnold, Abstr., 1888, 1179) with sodium ethoxide and ethyl iodide in absolute alcoholic solution in a reflux apparatus, is a yellow, mobile oil, which distils without decomposition at 134° under 14 mm. pressure, and is hydrolysed by concentrated alcoholic potassium hydroxide to oxalic and α-methylbutyric acids; by dilute sulphuric acid principally to carbon dioxide and methylethylpyruvic acid.

Methylethylpyruvic [*β-methyl-α-pentanonoic*] *acid*, $CHMeEt \cdot CO \cdot CO_2H$, forms white crystals, melts at 30·5°, boils at 90° under 12 mm. pressure, and is easily volatile in a current of steam; the *silver* and *calcium* ($+ 2H_2O$) salts crystallise in white leaflets. The *phenylhydrazone*, $C_{12}H_{16}O_2N_2$, crystallises in slender, yellow needles and melts at 130°. When reduced with sodium amalgam in aqueous solution in presence of carbon dioxide, methylethylpyruvic acid yields *β-methyl-β-ethyl-lactic acid* [*α-hydroxy-β-methylvaleric acid*], $CHMeEt \cdot CH(OH) \cdot CO_2H$, which forms white crystals, melts on the hand, and deliquesces rapidly when exposed to the air; the *silver* and *zinc* ($+ 2H_2O$) salts are described. When heated with 90 per cent. sulphuric acid at 70° in a reflux apparatus, α-hydroxy-β-methylvaleric acid yields carbon monoxide and a brown oil which has no aldehyde properties. G. Y.

New Method of Preparation of Esters of Mesoxalic Acid. Condensation with Esters of Cyanoacetic Acid. Ch. Schmitt (*Compt. rend.*, 1905, **140**, 1400—1401. Compare Abstr., 1904, ii, 42; Bouveault and Wahl, Abstr., 1904, i, 556).—Esters of mesoxalic acid are obtained with a yield of 60 per cent. when the corresponding malonic esters mixed with acetic anhydride and ether are subjected to the action of a current of the nitrous gas evolved by the action of water on acid nitrosyl sulphate. Methyl and ethyl mesoxalates were thus prepared. When ethyl mesoxalate (1 mol.) condenses with ethyl-cyanoacetate (1 mol.) in presence of piperidine, *ethyl cyanoethylenetricarboxylate*, $C(CO_2Et)_2 \colon C(CN) \cdot CO_2Et$, is obtained. It can be recrystallised from ether or light petroleum and melts at 25—26°. When condensation takes place between one molecule of the mesoxalate and two molecules of the cyanoacetate, *ethyl αγ-dicyanopropane-αββγ-tetracarboxylate*, $C(CO_2Et)_2[CH(CN) \cdot CO_2Et]_2$, is obtained. It melts at 103° and is only slightly soluble in ether or cold alcohol. If a solution of this substance in 85 per cent. alcohol is subjected to the action of a current of hydrogen chloride, a substance of the composition $C_{24}H_{31}O_{12}N_3$, melting at 99°, is obtained on evaporation. The formation of this substance is represented by the equation

$$2C_{15}H_{18}O_8N_2 + 5H_2O = C_{24}H_{31}O_{12}N_3 + 3CH_3 \cdot OH + 3CO_2 + NH_3.$$

Molecular weight found 553 (theory 545).

If ethyl dicyanopropanetetracarboxylate in alcoholic solution is treated with a current of ammonia, a substance, $C_{23}H_{25}O_{11}N_3$, is obtained which melts at 105—106°. Molecular weight found 516 (theory 519). H. M. D.

[Formula for Aldehyde Hydrogen Sulphites.] Arthur Rosenheim (*Ber.*, 1905, **38**, 2005).—A correction (compare Reinking, Dehnel, and Labhardt, this vol., i, 261, and Rosenheim and Sarow, this vol., i, 404). W. A. D.

Condensation of Synthetical *iso*Valeraldehyde with Formaldehyde. Richard Lichtenstern (*Monatsh.*, 1905, **26**, 497—504).—The *aldol*, $CPr^{\beta}(CH_2 \cdot OH)_2 \cdot COH$, formed by the action of 1 mol. of *iso*valeraldehyde on 2 mols. of formaldehyde in presence of potassium carbonate, is obtained as an oil which decomposes when warmed under 15 mm. pressure. The *oxime*, $C_7H_{14}O_2{:}NOH$, forms clusters of crystals, melts at 93°, and when boiled with acetic anhydride yields the *diacetylnitrile*, $CPr^{\beta}(CH_2 \cdot OAc) \cdot CN$, which is a yellow liquid boiling at 165—168° under 18 mm. pressure. The aldol is reduced, by aluminium amalgam in aqueous-alcoholic solution, to the *trihydric alcohol*, $CPr^{\beta}(CH_2 \cdot OH)_3$, which is a viscid liquid boiling at 156—158° under 15 mm. pressure. The *triacetate*, $C_{13}H_{22}O_6$, is a colourless, viscid liquid which boils at 168—170° under 15 mm. pressure. G. Y.

Compounds of Ketones with Ammonia. Methyl Ethyl Ketone Ammonia. Carl Thomae (*Arch. Pharm.*, 1905, **243**, 291—294, 294—296).—When a mixture of methyl ethyl ketone with twice its volume of alcohol is saturated with ammonia at intervals during several weeks, being kept in the dark meanwhile, and the product is allowed to evaporate in the air, *methyl ethyl ketone ammonia* remains as an oil with a composition corresponding with the formula $CMeEt(N{:}CMeEt)_2$. In one experiment, which lasted $\frac{3}{4}$ year, the yield was 77 per cent. of the theoretical. The substance appears to form salts with hydrochloric, oxalic, and picric acids, but the salts are very unstable. C. F. B.

Use of Oximino-ethers in Condensations. Otto Diels and Georg Plaut (*Ber.*, 1905, **38**, 1917—1921. Compare Abstr., 1903, i, 400).—The condensation between ethyl oxalate and β-diketones or their monoximes does not take place at all readily, but is considerably facilitated by the conversion of the monoxime into its methyl ether.

A good yield of the *methyl* ether of α-iso*nitrosomethyl propyl ketone* $COMe \cdot CEt{:}N \cdot OMe$, is obtained when an aqueous alkaline solution of the *iso*nitroso-compound is shaken with methyl iodide for 15 hours at 100°. It is a colourless liquid distilling at 53—54° under 32 mm. pressure, and readily condenses with ethyl oxalate in the presence of ether and sodium ethoxide (free from alcohol), yielding *ethyl δ-methyloximino-αγ-diketoheptoate*, $OMe \cdot N{:}CEt \cdot CO \cdot CH_2 \cdot CO \cdot CO_2Et$, which crystallises from light petroleum in stout, glistening needles melting at 40—41° and dissolving readily in most organic solvents.

Alcoholic sodium ethoxide hydrolyses the ester, yielding *δ-methyloximino-αγ-diketoheptoic acid*, $C_8H_{11}O_5N$, the *sodium* salt of which has an intense orange-yellow colour. J. J. S.

Relationships between Carbohydrates and the Nitrogenous Products of Metabolism. Franz Knoop and Adolf Windaus (*Beitr. chem. Physiol. Path.*, 1905, **6**, 392—395).—5-Methyliminazole, $\begin{matrix} CMe \cdot NH \\ \| \\ CH \text{---} N \end{matrix} \!\!> CH$, is formed when a solution of dextrose is exposed to sunlight at the ordinary temperature in presence of the strongly dissociated compound $Zn(OH)_2,4NH_3$. It is highly probable that methyl-

glyoxal and formaldehyde are produced as intermediate products and then react with the ammonia: $C_3H_4O_2 + CH_2O + 2NH_3 = C_4H_6N_2 + 3H_2O$. The conversion of dextrose into lactic acid by means of alkali hydroxides also consists in the intermediate formation of methylglyoxal (compare also Buchner and Meisenheimer, this vol., ii, 274).

The iminazole ring formation in plants may also occur in an analogous manner, for example, pilocarpine (Pinner, Abstr., 1902, i, 232, 638), histidine (Pauly, Abstr., 1904, i, 1068). The formation of purine derivatives may be of a similar nature. J. J. S.

Formation of Saccharins from Hexoses. ADOLF WINDAUS (*Chem. Zeit.*, 1905, **29**, 564. Compare Windaus and Knoop, this vol., i, 381).—Hexoses are decomposed by alkali hydroxides to two triose molecules, to a tetrose and glycolaldehyde, or to a pentose and formaldehyde, depending on the experimental conditions and the configuration of the hexose. The formation of saccharin has been explained by Kiliani as due to change of one triose molecule into lactic acid, and subsequent condensation of the unchanged aldehyde group with the α-C·OH group of the acid. The formation of parasaccharin (a) and of *iso*saccharin (b) may take place in the same manner, the acid being formed by isomeric change of the tetrose or of the pentose respectively:

(a) $OH{\cdot}CH_2{\cdot}COH + OH{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2H =$
$OH{\cdot}CH_2{\cdot}CH(OH){\cdot}C(OH)(CO_2H){\cdot}CH_2{\cdot}CH_2{\cdot}OH$;

(b) $CH_2O + OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2H =$
$OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}C(OH)(CO_2H){\cdot}CH_2{\cdot}OH$.

In the formation of metasaccharin, the hexose undergoes Wolf's change without rupture of the carbon chain: $OH{\cdot}CH_2{\cdot}[CH{\cdot}OH]_4{\cdot}COH \longrightarrow OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2H$.

The formation of saccharonic acid from glycuronic acid is explained, on the same principle, by the scheme:

$CO_2H{\cdot}[CH{\cdot}OH]_4{\cdot}COH \longrightarrow CO_2H{\cdot}CH(OH){\cdot}COH + OH{\cdot}CHMe{\cdot}CO_2H \longrightarrow CO_2H{\cdot}CH(OH){\cdot}CH(OH){\cdot}CMe(OH){\cdot}CO_2H$. G. Y.

Circumstances which Influence the Physical Condition of Starch. JULES WOLFF and AUGUSTE FERNBACH (*Compt. rend.*, 1905, **140**, 1403—1406. Compare this vol., i, 312).—Starch paste prepared from potato starch is always acid to phenolphthalein and alkaline to helianthin. From the same sample of starch two pastes were prepared, distilled water being used in one case (A), ordinary supply water in the other (B). On account of the basic properties of the dissolved calcium carbonate in the supply water, the paste B was found to be less acid to phenolphthalein, and more alkaline to helianthin than the paste A. When the two pastes, each containing 4·6 per cent. of starch, were heated at 120° for half an hour and then allowed to cool, the viscosity of A was found to be much smaller than that of B. That the difference in viscosity is essentially connected with the difference in the reaction towards phenolphthalein and helianthin was shown by the fact that the viscosity of the paste A could be considerably increased by adding small quantities of calcium (sodium, potassium) carbonate to the distilled water used in its preparation.

In another experiment, the starch before being used in the prepara-

tion of the paste was treated with very dilute hydrochloric acid in order to extract the small quantity of calcium salts present, and was then carefully washed with distilled water. The paste prepared from such starch, after heating at 120° for half an hour, was found to be much less viscous than the paste A.

The observations indicate that the small quantities of salts of the alkali and alkaline earth metals which accompany starch exert a very considerable influence on the physical properties of the pastes obtained from it and are of primary importance in connection with the phenomena of liquefaction and coagulation. H. M. D.

Constitution, Saccharification and Reversion of Starch Paste. Léon Maquenne and Eugène Roux (*Compt. rend.*, 1905, **140**, 1303—1308. Compare Abstr., 1903, i, 679; 1904, i, 17, 227, 294; this vol., i, 262, 328, and Fernbach and Wolff, Abstr., 1904, i, 374; 1905, i, 164, 312).—It is shown that natural starch grains consist of two substances, the principal one being amylocellulose, which is partially soluble in water at 100° and entirely soluble when heated with water under pressure. This substance in solution gives the characteristic blue colour with iodine, and is transformed integrally into dextrose by malt diastase, but in the solid state is unaffected by either of these reagents. Amylocellulose may exist in either the liquid (soluble) or solid (insoluble) state within a certain range of temperature and in presence of excess of water. The liquid form is produced by heating with water under pressure, and the solid form (which may be a kind of crystalline form of the substance, or a polymeride of the liquid form) by cooling the solution so produced. The separation of the solid form under the latter condition is what has so far been known as "reversion."

The second constituent is *amylopectin*, a mucilaginous substance, which gives no colour with iodine and dissolves in extract of malt without producing a reducing sugar. The gelatinisation of starch by boiling water or alkalis is due to the presence of amylopectin, and the initial liquefaction of starch paste on the addition of malt extract is due to the action of a liquefying enzyme (*amylopectinase*) contained in the malt extract in addition to ordinary diastase (amylase). "Artificial" starch differs from the natural material only in the absence of amylopectin. The presence of amylopectin retards the separation of the solid form of amylocellulose (reversion) both in the starch grain and in starch paste. T. A. H.

Acetyl Derivatives of Starch and Cellulose. Charles F. Cross, Edward J. Bevan, and John Traquair (*Chem. Zeit.*, 1905, **29**, 527—528. Compare Trans., 1904, **85**, 691).—The extent of the action of glacial acetic acid on starch at 100—105° is proportional to the time of heating and to the ratio between acid and carbohydrate. The acetyl compounds formed during the earlier stages of the action are insoluble in water, whilst those formed at the later stages are soluble.

The action of glacial acetic acid on cellulose is similar to that on starch. A. McK.

Formation of Sulphuric Esters in the Nitration of Cellulose and their Influence on Stability. C. NAPIER HAKE and REGINALD J. LEWIS (*J. Soc. Chem. Ind.*, 1905, **24**, 374—378).—The authors have made a number of experiments with a view to determining the causes which are responsible for the deterioration of explosives containing gun-cotton; they attribute the deterioration to the presence of sulphuric esters of cellulose derived from the latter by replacement of hydroxyl groups by the group $-SO_4H$ (compare Cross, Bevan, and Jenks, Abstr., 1901, i, 672). They draw the conclusion that sulphuric acid chemically combines with cellulose during nitration to form esters which decompose into esters of a more stable character, partly by hydrolysis during washing, and partly during storage of the finished product. The difficulty of eliminating these esters explains the erratic behaviour frequently observed in explosives exposed to tropical climatic conditions. P. H.

Acetosulphates of Cellulose. CHARLES F. CROSS, EDWARD J. BEVAN, and JOHN F. BRIGGS (*Ber.*, 1905, **38**, 1859—1865. Compare Abstr., 1901, i, 672).—Air-dried cotton wool (16 grams) is stirred for 20 minutes with 100 c.c. of a mixture containing equal parts of glacial acetic acid and acetic anhydride and 4·5 per cent. of sulphuric acid at 30°; after one hour, the reaction-mixture is poured into water, when the *hydrate* of "normal" cellulose acetosulphate separates as a semi-transparent, gelatinous mass, which, after drying in air at the ordinary temperature, contains about 8 per cent. of moisture, is completely soluble in warm alcohol, and decomposes with formation of sulphuric acid on prolonged heating or warming with alcohol. "Normal" *cellulose acetosulphate*, $(C_6H_7O_2)_4(OAc)_{10}SO_4$, obtained by drying the hydrate carefully at 90°, is hydrolysed by potassium hydroxide in 93 per cent. alcohol, forming *cellulose sulphate*, which is soluble in water.

If more than 5 per cent. of sulphuric acid is present in the acetic acid-anhydride mixture, a soluble *hydrate* is formed along with the hydrate of the normal ester. This has colloidal properties, can be obtained as a gelatinous precipitate by salting out, and contains a larger proportion of SO_4 than does the normal ester. If less than 4 per cent. of sulphuric acid is used, an *acetosulphate* is formed which contains less SO_4 than the normal ester, and is insoluble in alcohol but soluble in acetone. G. Y.

Employment of Metal-ammonium Compounds in Organic Chemistry; Formation of Primary Amines. PAUL LEBEAU (*Compt. rend.*, 1905, **140**, 1264—1266. Compare this vol., i, 401).—The reaction between the metal-ammonium compounds and the halogen derivatives of the fatty hydrocarbons probably takes place in two stages. In the first stage, the metal-ammonium compound is converted into the corresponding amide and this then reacts with another molecule of the halogen compound with the formation of a primary amine. For the reaction between methyl chloride and sodammonium the equations are: $CH_3Cl + 2NaNH_3 = CH_4 + NaNH_2 + NaCl + NH_3$; $CH_3Cl + NaNH_2 = CH_3{\cdot}NH_2 + NaCl$. In accordance with this, it is

found that whereas sodamide has no action on the alkyl haloids at the ordinary temperature, reaction readily takes place in liquid ammonia. The quantitative investigation of the reaction between sodamide and normal propylamine shows that these react in molecular proportions in accordance with the second equation. H. M. D.

Reaction of Ammonia with Commercial Calcium Carbide. ROBERTO SALVADORI (*Gazzetta*, 1905, **35**, i, 236—240. Compare Abstr., 1903, i, 11).—At a temperature of about 650°, calcium carbide and ammonia begin to react according to the equation $CaC_2 + 4NH_3 = CaCN_2 + NH_4CN + 4H_2$. The reaction takes place in two stages, in the first of which the calcium carbide and the nitrogen formed by the decomposition of the ammonia interact forming calcium cyanamide: $CaC_2 + N_2 = CaCN_2 + C$. The carbon thus liberated then acts on the ammonia, giving ammonium cyanide and hydrogen. The sample of carbide employed in the author's experiments contained only 78·22 per cent. of calcium carbide, the principal impurities being sulphur, silica, aluminium, iron, and magnesium, with traces of phosphorus, nitrogen, and carbon in the form of graphite; the residue insoluble in hydrochloric acid amounted to 1·73 per cent. T. H. P.

Guanidine Picrolonate. MARTIN SCHENCK (*Zeit. physiol. Chem.*, 1905, **44**, 427).—It is possible to separate guanidine from arginine and histidine by the use of picrolonic acid, guanidine picrolonate,

$$CN_3H_5{\cdot}C_{10}H_8N_4O_5,$$

being relatively soluble in alcohol. W. D. H.

Explosive Mercury Compounds. KARL A. HOFMANN (*Ber.*, 1905, **38**, 1999—2005. Compare Abstr., 1898, i, 635; 1899, i, 97, 485; 1900, i, 383, 384, 618).—*Chloratodimercuracetaldehyde*,

$$ClO_3{\cdot}Hg{\cdot}CHg{\cdot}CHO,$$

obtained by adding alcoholic acetaldehyde to a solution of mercuric oxide in aqueous chloric acid, crystallises in colourless, lustrous prisms and is exceedingly explosive, even when covered with water; on warming with sodium hydroxide and potassium cyanide, it gives the characteristic smell of aldehyde resin. *Chloratotrimercuracetaldehyde*,

$$ClO_3{\cdot}Hg{\cdot}C(Hg_2O){\cdot}CHO,$$

obtained by passing acetylene into an aqueous solution of mercuric chlorate or of a mixture of mercuric nitrate and sodium chlorate, is slightly less explosive, and when digested with 3 per cent. hydrochloric acid gives *trichloromercuracetaldehyde*, $C_2HHg_3Cl_3O$. *Perchloratomercuracetaldehyde*, obtained by passing acetylene into an aqueous solution of mercuric perchlorate, is less sensitive to shock than the corresponding chlorate.

Pyridine gives with an aqueous solution of mercuric chlorate the additive *compound*, $2C_5H_5N,Hg(ClO_3)_2$, which crystallises in colourless needles; the *perchlorate*, $2C_5H_5N,Hg(ClO_4)_2$, forms concentric aggregates of thick needles. Both these salts explode when heated, but are not sensitive to shock; they are at once decomposed by aqueous sodium hydroxide.

On passing acetylene into an aqueous solution of mercury potassium nitrite, a reddish-yellow precipitate having the composition $C_4H_6Hg_3O_6N_2$ is obtained; its nature is uncertain. Using a solution of mercuric nitrate with an excess of potassium nitrite in ice-cold water containing 1 per cent. of nitric acid, *nitritodimercuracetaldehyde*, $NO_2 \cdot Hg \cdot CHg \cdot CHO$, is obtained as a bright yellow explosive powder; that the product is a nitrite is shown by its behaviour with sulphanilic acid or α-naphthylamine in presence of acetic acid and hydrochloric acid. W. A. D.

Derivatives of *cyclo*Butane. RICHARD WILLSTÄTTER and WOLFGANG VON SCHMAEDEL (*Ber.*, 1905, 38, 1992—1999).—cyclo*Butyltrimethylammonium iodide*, $CH_2{<}{CH_2 \atop CH_2}{>}CH \cdot NMe_3I$, obtained by methylating *cyclo*butylamine, crystallises from acetone in slender, white needles and decomposes at 256—257°. When the corresponding *hydroxide*, $CH_2{<}{CH_2 \atop CH_2}{>}CH \cdot NMe_3 \cdot OH$, is distilled, it gives a mixture of cyclo*butene*, ${CH_2 \cdot CH \atop CH_2 \cdot CH}$, trimethylamine, methyl alcohol, and cyclo*butyldimethylamine*, $CH_2{<}{CH_2 \atop CH_2}{>}CH \cdot NMe_2$; the latter boils at 97—98° (corr.) and gives a well-defined *aurichloride* and *picrate*. The cyclo*butene* is a gas which is absorbed by chloroform and combines additively with bromine, forming the *dibromide*, $C_4H_6Br_2$, which boils at 69·5° under 24 mm. and at 171—174° (corr.) under the ordinary pressure, solidifies at −2°, and melts at 1—4°; the liquid has a sp. gr. 1·972 at 0°/4° and does not readily combine with aliphatic amines. Some αδ-butadiene dibromide, $CH_2Br \cdot CH{:}CH \cdot CH_2Br$ (Thiele, Abstr., 1900, i, 2), is formed together with the foregoing dibromide, and may be separated from it by the action of dimethylamine, which converts it into *αδ-tetramethyldiamino-Δ^β-butene*,

$$NMe_2 \cdot CH_2 \cdot CH{:}CH \cdot CH_2 \cdot NMe_2;$$

this boils at 39—40° under 24—25 mm. and at 166—169° (corr.) under the ordinary pressure.

cyclo*Butene dibromide* is attacked by quinoline only at high temperatures, when red condensation products are principally formed; a little butadiene is evolved. On heating *cyclo*butene dibromide with powdered potassium hydroxide at 100—105°, *Δ¹-bromo*cyclo*butene*, ${CBr{:}CH \atop CH_2 \cdot CH_2}$, is obtained; it boils at 92·5—93·5° (corr.), has a sp. gr. 1·524 at 0°/4°, and on oxidation with potassium permanganate in neutral alcoholic solution, followed by oxidation of the intermediate product with chromic acid, gives succinic acid. The oxidation probably takes place thus:

$${CBr{:}CH \atop CH_2 \cdot CH_2} \longrightarrow {OH \cdot CBr \cdot CH \cdot OH \atop CH_2 \cdot CH_2} \longrightarrow {CO{-}CO \atop CH_2 \cdot CH_2} \longrightarrow {CO_2H \;\; CO_2H \atop CH_2{-}CH_2}.$$

When *cyclo*butene dibromide is heated with potassium hydroxide above 210°, acetylene is the principal product. W. A. D.

*cyclo*Octenes. Richard Willstätter and Hans Veraguth (*Ber.*, 1905, **38**, 1975—1984).—On methylating *des*-dimethylgranatanine (this vol., i, 543), decomposing the resulting methiodide with silver oxide, and distilling the quaternary base,

$$CH\lessdot\!\begin{matrix}CH_2\cdot CH_2\cdot CH_2\\ CH-CH_2\cdot CH_2\end{matrix}\!\gtrdot CH\cdot NMe_3\cdot OH,$$

obtained, methylamine and water are eliminated, and a cyclo*octadiene*, C_8H_{12}, produced; it is a colourless oil, which boils at 39·5° under 16·5 mm. pressure, has a sp. gr. 0·889 at 0°/4°, decolorises potassium permanganate solution, and rapidly polymerises at the ordinary temperature. *Di*cyclo*octadiene*, $C_{16}H_{24}$, formed in this way, crystallises from light petroleum in rosettes of thin leaflets, softens at 106°, and melts at 114°; a second *polymeride*, $(C_8H_{12})_x$, is also formed, which is insoluble in ether, crystallises from xylene in microscopic cubes, and melts above 300°.

cyclo*Octadiene dibromide*, $C_8H_{12}Br_2$, obtained by gradually adding bromine dissolved in chloroform to *cyclo*octadiene dissolved in the same solvent, boils at 142—143° under 14 mm. pressure; *bromo*cyclo*octadiene*, $C_8H_{11}Br$, which is formed at the same time, boils at 93·5—94·5° under 17 mm. pressure. Attempts to prepare a *cyclo*octatriene, C_8H_{10}, by the action of quinoline on either of the foregoing bromo-derivatives, gave always mixtures of the diene and triene. By heating the crude dibromide with dimethylamine dissolved in benzene for five hours at 130—140°, a mixture of isomeric *dimethylamino*cyclo*octadienes*, $C_8H_{11}\cdot NMe_2$, is obtained, distilling between 64° and 79° under 11 mm. pressure; the derived *methiodides* differ in their solubility in alcohol. The more soluble methiodide yields a quaternary *base*, which on distillation gives a cyclo*octatriene*, C_8H_{10}, boiling at 36—40° under 13 mm. pressure.

It is probable that the hydrocarbons considered by Döbner (Abstr., 1902, i, 598; 1903, i, 149) to be *cyclo*octadiene and its derivatives are not really of this nature. W. A. D.

Nitration of Fluorobenzene. II. Arnold F. Holleman (*Rec. trav. Chim.*, 1905, **24**, 140—146).—The author has redetermined the relative proportions in which the *o*-, *m*-, and *p*-fluoronitrobenzenes are formed by the nitration of fluorobenzene under the conditions already described (Abstr., 1904, i, 486). *o*-Fluoronitrobenzene (compare M. Holleman, this vol., i, 424) can be estimated by conversion into *o*-nitroaniline by heating it in a sealed tube with a solution of ammonia, in presence of alcohol and calcium chloride (to prevent erosion of the tube by the ammonium fluoride formed), the *meta*-isomeride remaining almost unaffected by this treatment. The greater part of the *p*-fluoronitrobenzene is first separated from the crude product by crystallisation and the remainder estimated by conversion into *p*-nitroanisole as already described (*loc. cit.*). The crude nitration product was found to contain 87·4 per cent. of *p*-fluoronitrobenzene, 12·4 per cent. of the ortho-isomeride, and 0·2 per cent. of the meta-compound. The inaccuracy of the results previously given is due to the assumption then made that, under the conditions employed, the

whole of the *p*-fluoronitrobenzene is converted into *p*-nitroanisole, which is now found not to be the case. T. A. H.

Two Aromatic Nitroso-compounds [*m*-Dinitrosobenzene and *m*-Nitronitrosobenzene]. FRIEDRICH J. ALWAY and ROSS A. GORTNER (*Ber.*, 1905, **38**, 1899—1901).—m-*Dinitrosobenzene*, $C_6H_4(NO)_2$, prepared by the reduction of *m*-dinitrobenzene in alcoholic solution with zinc dust and acetic acid below 0° and distilling the product with steam, forms a yellow powder melting at 146·5° to a green liquid and subsequently decomposing. The later fractions of the distillate yield crystals which are solid solutions of *m*-nitronitrosobenzene (Abstr., 1903, i, 690) in *m*-dinitrobenzene. E. F. A.

Oxidation of Naphthalene to Phthalic Acid by Concentrated Sulphuric Acid in presence of Oxides or Salts of Rare Metals. HUGO DITZ (*Chem. Zeit.*, 1905, **29**, 581—582).—A mixture of 25 grams of naphthalene, 375 grams of concentrated sulphuric acid, and 15 grams of the oxides formed by heating the oxalates of the rare metals obtained in the manufacture of thorium nitrate was heated in a retort. At 220°, there was a copious evolution of sulphur dioxide and carbon dioxide, and at 230° the liquid commenced to boil; at 230—300°, the distillate consisted of phthalic anhydride and a brown liquid, but above 300° of the anhydride only. A further quantity of phthalic anhydride was obtained by heating the liquid distillate with 5 grams of the oxide mixture. The yield of phthalic anhydride was not increased by the use of a greater proportion of the oxides, or by alteration of the order of mixing the naphthalene, sulphuric acid, and oxides.

The oxidation of naphthalene to phthalic anhydride takes place less easily, and probably with a smaller yield, in presence of the oxides of the rare metals than in presence of mercuric oxide, but the oxides of the rare metals are the more easily recovered from the reaction residue. G. Y.

Synthesis in the Anthracene Series. Condensation of Dihydro*iso*benzofuran Derivatives into 9:10-Substituted Anthracene Derivatives. ALFRED GUYOT and J. CATEL (*Compt. rend.*, 1905, **140**, 1460—1464. Compare this vol., i, 226).—1:1:2-Triphenyl-1:2-dihydro*iso*benzofuran is readily converted by the action of concentrated sulphuric acid into 9:10-diphenylanthracene, the following equations representing the probable course of the reaction:

$$C_6H_4{<}{\begin{matrix}CPh_2\\CHPh\end{matrix}}{>}O + H_2O \longrightarrow C_6H_4{<}{\begin{matrix}CPh_2{\cdot}OH\\CHPh{\cdot}OH\end{matrix}} \longrightarrow$$

$$2H_2O + C_6H_4{<}{\begin{matrix}CPh\\|\\CPh\end{matrix}}{>}C_6H_4.$$

1:2-Diphenyl-1:2-dihydro*iso*benzofuran and its isomeride, 1:1-diphenyl-1:2-dihydro*iso*benzofuran, similarly yield 9-phenylanthracene; 1:1:2-triphenyl-2-dimethylaminophenyldihydro*iso*benzofuran and its isomeride yield 9:9:10-triphenyl-10-dimethylaminophenyl-9:10-dihydroanthracene, which yields the two stereoisomeric forms of 9:10-tetramethyldiaminodiphenyl-9:10-diphenyldihydroanthracene

(compare this vol., i, 188, 270) on heating in acetic acid solution with dimethylaniline; *o*-benzhydryltriphenylcarbinol yields 9 : 10-diphenylanthracene; *o*-dibenzhydrylbenzene and its isomeride, the *carbinol*, $OH\cdot CH_2\cdot C_6H_4\cdot CPh_2OH$, yield 9-phenylanthracene.

The *carbinol*, $OH\cdot CH_2\cdot C_6H_4\cdot CPh_2\cdot OH$, is obtained from the phthalide by the action of magnesium phenyl bromide, and yields 1 : 1-*diphenyl*-1 : 2-*dihydro*iso*benzofuran*, $C_6H_4<\begin{matrix}CH_2\\CPh_2\end{matrix}>O$, on simple dehydration.

M. A. W.

Reduction of Nitro-derivatives with Sodium Hyposulphite. JULES ALOY and RABAUT (*Bull. Soc. chim.*, 1905, [iii], **33**, 654—655. Compare Abstr., 1904, i, 870, and this vol., i, 429).—The authors find that nitrobenzene, α-nitronaphthalene, *o*- and *p*-nitrophenols, and nitromethane can be reduced to the corresponding amines by the use of sodium hyposulphite. The latter reagent also reduces inorganic nitrites in presence of alkalis, forming ammonia, but does not attack nitrates.

T. A. H.

Amino*cyclo*propane. NIC. M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 304—317. Compare Abstr., 1901, i, 509).—Amino*cyclo*propane, obtained previously by the author (*loc. cit.*), has been further studied. It boils at 49·5—50° under 760 mm. pressure, has the sp. gr. 0·8343 at 0°/0° and 0·8131 at 20°/0° and n_D 1·4210 at 20°. The *hydrobromide*, $C_3H_5\cdot NH_2,HBr$, is readily soluble in water or alcohol, and crystallises from the latter alone or mixed with ether in needles melting at 153·5—155°. The *aurichloride*, $C_3H_8NCl,AuCl_3,H_2O$, crystallises in quadratic plates readily soluble in water. The corresponding *benzenesulphonamide*, $\begin{matrix}CH_2\\|\\CH_2\end{matrix}>CH\cdot N(SO_2Ph)_2$, crystallises from alcohol in prismatic needles melting at 119·5—120°. *Benzoylamino*cyclo*propane*, $C_3H_5\cdot NHBz$, crystallises from methyl or ethyl alcohol in long needles melting at 98·5°.

*Phenyl*cyclo*propylcarbamide*, $NHPh\cdot CO\cdot NH\cdot CH<\begin{matrix}CH_2\\|\\CH_2\end{matrix}$, crystallises from methyl alcohol in prismatic needles melting at 153°.

*Phenyl*cyclo*propylthiocarbamide*, $NHPh\cdot CS\cdot NH\cdot C_3H_5$, separates from methyl alcohol in many-faced crystals melting at 123—123·5° and dissolves readily in benzene, but only slightly in light petroleum.

At the ordinary temperature, an aqueous solution of amino*cyclo*propane readily reduces freshly precipitated silver oxide suspended in water, and alkaline permanganate is rapidly decolorised by it. Oxidation of amino*cyclo*propane with chromic acid yields acraldehyde, but if the oxidation is effected in presence of sulphuric acid, only ethylene and carbon dioxide are formed, the reaction in this case being probably expressed by the scheme:

$$\begin{matrix}CH_2\\|\\CH_2\end{matrix}>CH\cdot NH_2 \longrightarrow \begin{matrix}CH_2\\|\\CH_2\end{matrix}>CO \longrightarrow \begin{matrix}CH_2\cdot CO\\|\quad\quad|\\CH_2\cdot O\end{matrix} \longrightarrow \begin{matrix}CH_2\\||\\CH_2\end{matrix} + CO_2.$$

Treatment of the amine with nitrous acid yields allyl alcohol.

T. H. P.

Hydrofluorides of some Anilides and Substituted Anilines. RUDOLF F. WEINLAND and H. LEWKOWITZ (*Zeit. anorg. Chem.*, 1905, 45, 39—51).—The following, mostly well-crystallised, strongly acid substances, were prepared: from acetanilide, NHPhAc,HF; from *p*-acetotoluide, $C_6H_4Me\cdot NHAc,HF$; from benzanilide, NHPhBz,HF; from *p*-hydroxyacetanilide, $OH\cdot C_6H_4\cdot NHAc,3HF,2H_2O$; from *p*-methoxyacetanilide, $OMe\cdot C_6H_4\cdot NHAc,HF$; from *p*-ethoxyacetanilide, $OEt\cdot C_6H_4\cdot NHAc,HF,H_2O$ and also $OEt\cdot C_6H_4\cdot NHAc,3HF,2H_2O$; from *p*-bromoacetanilide, $C_6H_4Br\cdot NHAc,HF,H_2O$. In air, these substances lose hydrofluoric acid, and in pure water or alcohol dissociation is complete. The following crystalline hydrofluorides of the parent amines of the above anilides were prepared: (1) from aniline, $NH_2Ph,HF,1\frac{1}{2}H_2O$, $NH_2Ph,2HF$, and $NH_2Ph,3HF,\frac{1}{2}H_2O$; (2) from *p*-aminophenol, $OH\cdot C_6H_4\cdot NH_2,3HF,1\frac{1}{2}H_2O$; (3) from *p*-aminophenetole, $OEt\cdot C_6H_4\cdot NH_2,2HF$; (4) from *p*-aminobenzoic acid,

$$NH_2\cdot C_6H_4\cdot CO_2H,2HF;$$

(5) from *p*-bromoaniline, $C_6H_4Br\cdot NH_2,3HF,H_2O$; (6) from *o*-, *m*-, or *p*-nitroaniline, $NO_2\cdot C_6H_4\cdot NH_2,3HF,H_2O$. D. H. J.

[Thioanilines.] OSCAR HINSBERG (*Ber.*, 1905, 38, 1901—1902). —The author emphasises that, as previously shown (this vol., i, 339), on fusing together aniline, aniline hydrochloride, and sulphur at 170—180° a mixture is obtained of diphenylamine, dithioaniline, melting at 76—77°, Merz's thioaniline, and a thioaniline melting at 58° (compare Hofmann, this vol., i, 427). The colourless dithioaniline described by Hofmann (Abstr., 1895, i, 132), melting at 80° and forming an acetate melting at 205°, is not identical with the yellow dithioaniline, which melts at 76—77° and forms an acetate melting at 182°.
E. F. A.

Action of Aniline on Ethylcarbylamine Dibromide. H. GUILLEMARD (*Bull. Soc. chim.*, 1905, [iii], 33, 652—654. Compare Abstr., 1904, i, 563).—When aniline, dissolved in chloroform, is added to a solution of ethylcarbylamine dibromide in the same solvent, aniline hydrobromide is precipitated, and, on evaporating the mother liquor and washing the residue with ether, *diphenylethylguanidine hydrobromide* is obtained, which crystallises in colourless needles, melts at 180—182°, and, on treatment with potassium hydroxide and subsequent extraction with ether, yields the free *base*, $NEt\colon C(NHPh)_2$, in the form of a viscous, faintly yellow, alkaline syrup, which boils and decomposes at 145—147° under 50 mm. pressure.

Diphenylethylguanidine reacts with carbon disulphide, forming *s*-diphenylthiocarbamide and ethylthiocarbimide, and with water only, at 250°, yielding diphenylcarbamide and ethylamine with the secondary products aniline and carbon dioxide; with solution of potassium hydroxide in water, the hydrolysis goes more easily and no secondary products are formed.

Ethylcarbylamine dibromide reacts in a similar manner with other primary and secondary amines. T. A. H.

Products of the Action of Magnesium Organic Compounds on Alkylidene Bases. MAX BUSCH and ARTHUR RINCK (*Ber.*, 1905, **38**, 1761—1772. Compare Abstr., 1904, i, 663).—When α-anilinoethylbenzene, NHPh·CHPhMe, is oxidised in acetone solution with potassium permanganate, a yellow oil is obtained, which is probably *acetophenoneanil*, NPh:CMePh, as it is rapidly decomposed by dilute sulphuric acid into aniline and acetophenone. On heating α-anilinoethylbenzene hydrochloride with aniline hydrochloride at 210—220°, it is transformed into p-*aminodiphenylethane*, $CHMePh·C_6H_4·NH_2$, a brown oil, which gives a *sulphate* crystallising in white needles and melting at 206—207°; the *benzoyl* derivative, $CHMePh·C_6H_4·NHBz$, crystallises from alcohol in white leaflets and melts at 128°.

α-*Anilinopropylbenzene*, NHPh·CHEtPh, prepared from benzylideneaniline and magnesium ethyl iodide, forms a slightly yellow, viscid oil and boils at 192° under 20 mm. pressure; the *nitrate*, $C_{15}H_{17}N,HNO_3$, crystallises in transparent needles or prisms and melts at 174°; the *hydrochloride* forms long, white needles and melts at 187°.

α-*Anilinobutylbenzene*, $NHPh·CHPr^{a}Ph$, prepared from benzylideneaniline and magnesium propyl iodide, boils at 200° under 20 mm. pressure; the *nitrate* forms large, colourless crystals melting at 168°; the *hydrochloride* forms slender, white, silky needles and melts at 205°.

α-*Anilino*iso*hexylbenzene*, $NHPh·CHPh·CH_2·CH_2Pr^{\beta}$, prepared from benzylideneaniline and magnesium *iso*amyl iodide, boils at 212—215° under 20 mm. pressure and forms a viscid oil with a blue fluorescence; the *nitrate* crystallises from dilute alcohol in white needles and melts at 155°; the *hydrochloride* melts at 206°.

α-*Anilino-αβ-diphenylethane*, $NHPh·CHPh·CH_2Ph$, from benzylideneaniline and magnesium benzyl chloride, crystallises from alcohol in colourless, prismatic needles, melts at 56°, and boils at 247—248° under 18 mm. pressure; the *nitrate* forms colourless, prismatic crystals and melts at 132°; the *hydrochloride* forms aggregates of needles, melts at 192°, and when heated with aniline hydrochloride is transformed largely into stilbene, p-*aminotriphenylethane*,

$$CH_2Ph·CHPh·C_6H_4·NH_2,$$

being formed only to the extent of 10 per cent. of the theoretical quantity; the *hydrochloride* of the base crystallises in colourless needles and melts at 230°.

Anilinodiphenylmethane, $NHPh·CHPh_2$, prepared from benzylideneaniline and magnesium phenyl bromide, crystallises from absolute alcohol in colourless, prismatic needles, melts at 58°, and boils at 232—234° under 20 mm. pressure; the *nitrate* melts at 160°. When the hydrochloride of the base is heated with aniline hydrochloride for 6 hours at 210°, *p*-aminotriphenylmethane is obtained with a yield of 85 per cent. of the theoretical.

p-*Toluidinodiphenylmethane*, $CHPh_2·NH·C_6H_4Me$, prepared from benzylidene-*p*-toluidine and magnesium phenyl bromide, crystallises from absolute alcohol in lustrous prisms, melts at 91°, and boils at 237—238° under 15 mm. pressure; the *hydrochloride* forms slender, white needles and melts at 196°. o-*Toluidinodiphenylmethane*, prepared in a similar manner from benzylidene-*o*-toluidine, crystallises from absolute alcohol in short prisms, melts at 84°, and boils at 228—234°

under 12 mm. pressure; the *hydrochloride* forms sheaves of thick needles, melts at 142°, and when heated with *o*-toluidine hydrochloride gives *diphenyl*-p-*aminotolylmethane*, $CHPh_2\cdot C_6H_4Me\cdot NH_2$. This base is isolated in the form of the *sulphate*, which crystallises from alcohol or dilute sulphuric acid in slender, white needles and melts at 151°. *Tolyldiphenyl*-p-*benzoylaminomethane* crystallises from alcohol in small, white, transparent prisms and melts at 187°.

o-*Anisidinodiphenylmethane*, $CHPh_2\cdot NH\cdot C_6H_4\cdot OMe$, prepared from benzylidene-*o*-anisidine and magnesium phenyl bromide, crystallises from alcohol in transparent prisms, melts at 92°, boils at 244—245° under 15 mm. pressure, and gives a *hydrochloride* crystallising from alcohol in needles and melting at 162°. p-*Anisidinodiphenylmethane*, prepared similarly from benzylidene-*p*-anisidine, crystallises from alcohol in sheaf-like aggregates of needles, melts at 81°, and boils at 252—255° under 12 mm. pressure; the *hydrochloride* melts at 187° and the *nitrate* at 153°.

*a-Anilino-a-*p-iso*propylphenylethane*, $C_6H_4Pr^{\beta}\cdot CHMe\cdot NHPh$, prepared from cuminylideneaniline and magnesium methyl iodide, crystallises from dilute alcohol in long, colourless needles, melts at 59°, and boils at 200° under 15 mm. pressure; the *hydrochloride* crystallises from a mixture of alcohol and ether in thick needles and melts at 177°.

Anilinophenyl-a-naphthylmethane, $NHPh\cdot CHPh\cdot C_{10}H_7$, prepared from benzylideneaniline and magnesium *a*-naphthyl bromide, crystallises from a mixture of benzene and light petroleum, melts at 112°, and boils at 270° under 15 mm. pressure; the *hydrochloride* melts at 186°.

Magnesium methyl iodide seems to combine additively with phenylbenzylidenehydrazine, but the product could not be isolated owing to its decomposing in presence of water into aniline and acetophenone. W. A. D.

Asymmetric Nitrogen. XIX. EDGAR WEDEKIND (*Ber.*, 1905, **38**, 1838—1844).—The author has prepared *a*-phenylbenzylmethylallylammonium hydroxide from the corresponding active *a*-iodide, and finds that it has relatively constant rotatory power. If its aqueous-alcoholic solution is left either in the light or the dark, or if it is heated to 70°, no change occurs in the rotation. When the solution is boiled for two hours, however, the specific rotation diminishes considerably, owing to decomposition of the base. In a mixture of alcohol and water, the hydroxide has the specific rotation $[a]_D$ +75·5° at 18° and the molecular rotation $[M]_D$ +192·6°, which is very nearly identical with that of the corresponding active iodide, namely, +192° (see Pope and Peachey, Trans., 1899, **75**, 1127).

Ethylenedikairolinium di-d-*camphorsulphonate*,

$$C_{22}H_{30}N_2(C_{10}H_{15}O\cdot SO_3)_2,$$

crystallises from a mixture of alcohol and ether in almost colourless needles melting at 228°, and has $[a]_D$ +14·84°. On fractional precipitation of the alcoholic solution with ether, fractions were obtained giving for $[a]_D$ the values 14·84°, 12·39°, 13·42°, and 15·45°, and melting at 229°, 228°, 228°, and 224° respectively. Hence no resolution of the base takes place under these conditions; in fact, the ethylenedikairolinium dibromide prepared from the first of the above

fractions, after crystallisation from a mixture of alcohol and ether, is inactive.

*Ethylenedikairolinium di-*d*-bromocamphorsulphonate* was prepared and was separated into two fractions, of which the more sparingly soluble one was separated by crystallisation from a mixture of alcohol and ether into two fractions; the first (I) gives $[\alpha]_D$ +58·1° and $[M]_D$ +547·7°, and the second (II) $[\alpha]_D$ +56·08° and $[M]_D$ +528·3°. The molecular rotation of the *d*-bromocamphorsulphonic ion is + 270°, so that the active cation in fraction I has the $[M]_D$ +7·7°. On precipitating the concentrated solution of fraction I with potassium bromide, the ethylenedikairolinium dibromide obtained gave $[\alpha]_D$ +31·12° and $[M]_D$ + 150°, values which are much greater than would be arrived at from the molecular rotation of the *d*-bromocamphorsulphonate. By means of the bromocamphorsulphonate, an active base is hence obtained which contains two asymmetric nitrogen atoms and is of the type $(OH{\cdot}XYZ)N{\cdot}CH_2{\cdot}CH_2{\cdot}N(ZYX{\cdot}OH)$; this is being further studied.

It has not yet been settled whether isomerides are obtained when inactive tertiary bases with an asymmetric carbon atom are converted into asymmetric quaternary ammonium salts. The author has prepared *methylallyltetrahydroquinaldinium iodide*,

$$C_6H_4{<}\begin{matrix}CH_2\text{——}CH_2\\NMeI(C_3H_5)\end{matrix}{>}CHMe,$$

separating from a mixture of alcohol and ether in crystals decomposing at 154—155°, by the action of excess of allyl iodide on 1-methyltetrahydroquinaldine at the ordinary temperature. When the crude product is fractionally crystallised, the last mother liquors contain a readily soluble amorphous salt, which is possibly an isomeride. T. H. P.

The Constitution of Nitrosophenols and the Conception of ortho-, meta-, and para-Positions. Raymond Vidal (*Chem. Zeit.*, 1905, **29**, 486).—The substance obtained by the action of nitrous acid on phenol may react either as nitrosophenol or as quinoneoxime. It is reduced in alkaline solution into *p*-aminophenol, showing that in presence of alkali the nitrosophenol form is predominant, whereas reduction in acid solutions yields, together with a small quantity of *p*-aminophenol, an amorphous, dark brown, condensation product of the unstable quinoneimide, which is primarily formed by the reduction of the quinoneoxime.

The behaviour of cresols towards nitrous acid is discussed, and a theory of the configuration of substituted benzene derivatives is put forward to account for the influence of the methyl group. P. H.

Action of Bromine on the Anthranols. Carl Liebermann and Leonhard Mamlock (*Ber.*, 1905, **38**, 1797—1798).—On bromination with 1 mol. of bromine in carbon disulphide solution, anthranol gives rise to 10-bromoanthranol (Goldmann, Abstr., 1887, 1049); when this substance is digested with methyl or propyl alcohol for 4—5 hours at 100°, *dianthranol ether*, $\left(OH{\cdot}C{<}\begin{matrix}C_6H_4\\C_6H_4\end{matrix}{>}C\right)_2O$, is obtained in sparingly soluble crystals melting and decomposing at 235—250°.

Resorcinylanthranol, $OH\cdot C\begin{smallmatrix}\diagup C_6H_4 \diagdown \\ \diagdown C_6H_4 \diagup\end{smallmatrix}C\cdot C_6H_3(OH)_2$, prepared by heating 10-bromoanthranol with resorcinol in benzene solution, separates from alcohol saturated with sulphur dioxide on adding water saturated with the same gas in microscopic crystals, darkens at 150°, and melts and decomposes at 200°; the *triacetyl* derivative, $C_{26}H_{20}O_6$, crystallises from alcohol and melts at 181—183°; the alcoholic solution shows a strong blue fluorescence.

10-*Bromo*-1 : 9-*dihydroxyanthracene*, obtained by brominating 1 : 9-dihydroxyanthracene, forms yellow prisms and decomposes at about 120°. W. A. D.

meso-**Phenyl Derivatives of Anthracene.** CARL LIEBERMANN and SIMON LINDENBAUM (*Ber.*, 1905, **38**, 1799—1805. Compare Abstr., 1904, i, 901).—2' : 4'-*Dihydroxy*-9 : 9-*diphenyl*-10-*anthrone*, $CO{<}{\substack{C_6H_4\\C_6H_4}}{>}CPh\cdot C_6H_3(OH)_2$, prepared by heating phenylanthrone chloride with resorcinol and benzene, crystallises from dilute alcohol in long, colourless needles containing water of crystallisation and melts when dry at 259—261°; on acetylation, it gives the *diacetyl* derivative, $C_{30}H_{22}O_5$, which crystallises from absolute alcohol in thick, colourless plates and melts at 191—192°.

Phenylanthrone chloride combines with phenol in benzene solution, giving 10-*hydroxy*-9 : 10-*diphenoxy*-9-*phenyldihydroanthracene*,

$$OH\cdot C(OPh){<}{\substack{C_6H_4\\C_6H_4}}{>}CPh\cdot OPh,$$

which crystallises from glacial acetic acid in white, lustrous plates and melts at 251—252°; the *acetyl* derivative, $C_{34}H_{26}O_4$, crystallises from absolute alcohol in white needles and melts at 169—171°.

10-*Hydroxy*-9 : 10-*di*-o-*tolyloxy*-9-*phenyldihydroanthracene*, $C_{34}H_{28}O_3$, prepared in similar manner from *o*-cresol, crystallises from alcohol in thick, colourless plates and melts at 196—197°.

9-*Ethoxy*-9-*phenyl*-10-*anthrone*, $CO{<}{\substack{C_6H_4\\C_6H_4}}{>}CPh\cdot OEt$, obtained by boiling phenylanthrone chloride with absolute alcohol, crystallises from the latter in rhombic plates, and melts at 156—158°.

9 : 9-*Diphenyldihydroanthracene*, $CH_2{<}{\substack{C_6H_4\\C_6H_4}}{>}CPh_2$, obtained by reducing diphenylanthrone with zinc and acetic acid, crystallises from glacial acetic acid in colourless needles and melts at 195—196°.

2' : 4'-*Diacetoxy*-9 : 9-*diphenyldihydroanthracene*,

$$CH_2{<}{\substack{C_6H_4\\C_6H_4}}{>}CPh\cdot C_6H_3(OAc)_2,$$

prepared in similar manner by reducing the corresponding anthrone, crystallises from absolute alcohol in small needles and melts at 212—214°.

10-*Bromo*-9 : 9-*diphenyldihydroanthracene*, prepared by brominating at the ordinary temperature 9 : 9-diphenyldihydroanthracene dissolved in carbon disulphide, crystallises from glacial acetic acid or light petroleum in colourless needles and melts and decomposes at 214—216°; when water is added to its solution in boiling glacial

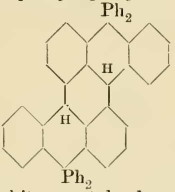
acetic acid, 10-*hydroxy*-9 : 9-*diphenyldihydroanthracene*,

$$OH\cdot CH<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CPh_2,$$

crystallising from absolute alcohol and melting at 240—241°, is obtained. 10-*Ethoxy*-9 : 9-*diphenyldihydroanthracene*,

$$OEt\cdot CH<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CPh_2,$$

obtained by boiling the 10-bromo-compound with alcohol, preferably in presence of potassium hydroxide, crystallises from absolute alcohol in rosettes of needles and melts at 158—159°. When 10-bromo-9 : 9-diphenyldihydroanthracene is boiled with naphthalene, it loses its bromine and gives *tetraphenylheptacyclene*,



which forms yellowish-white crystals, does not melt at 360°, and is insoluble in all solvents. W. A. D.

Phenylmethylethylene Oxide and its Conversion into Hydratropaldehyde. August Klages (*Ber.*, 1905, 38, 1969—1971).—*Phenylmethylethylene oxide*, $O<\begin{matrix}CMePh\\|\\CH_2\end{matrix}$, prepared by the action of sodium ethoxide on phenylmethylchloromethylcarbinol, $OH\cdot CMePh\cdot CH_2Cl$, is an oil, which boils at 85—87° under 17 mm. pressure. It is readily converted into hydratropaldehyde by the action of dilute sulphuric acid. When shaken with an aqueous solution of sodium hydrogen sulphite, it forms the sodium hydrogen sulphite compound of hydratropaldehyde, from which the aldehyde was isolated and identified by its boiling point, 98—100° under 16 mm. pressure, and by the formation of its semicarbazone melting at 153°.

The *benzhydrazone*, $COPh\cdot NH\cdot N:CH\cdot CHMePh$, separates from alcohol in glistening needles and melts at 191—192°.

The m-*nitrobenzhydrazone* melts at 156—157°. A. McK.

Methoethenylbenzene [Phenylmethylethylene] Oxide. Marc Tiffeneau (*Compt. rend.*, 1905, 140, 1458—1460. Compare Klages, preceding abstract).—Phenylmethylethylene oxide, $O<\begin{matrix}CPhMe\\|\\CH_2\end{matrix}$, prepared by the action of boiling aqueous potassium hydroxide or metallic sodium in ethereal solution on phenylmethylchloromethylcarbinol or by the action of powdered potassium hydroxide on an ethereal solution of the corresponding iodo-compound,

boils at 84—86° under 15 mm. pressure, has a sp. gr. 1·043 at 0°, and is converted into hydrotropaldehyde by distilling at 190—200°, or by the action of dilute acids, sodium hydrogen sulphite, or sulphurous acid (compare Abstr., 1902, i, 433, 666; also Bouveault, this vol., i, 116). Phenylmethylethylene oxide reacts with magnesium phenyl bromide to form the secondary *alcohol*, CHMePh·CHPh·OH, boiling at 185—190° under 20 mm. pressure. M. A. W.

Pinacone-pinacolin Rearrangement. P. J. Montagne (*Amer. Chem. J.*, 1905, **33**, 604—605).—In view of the work of Acree (this vol., i, 216), the author draws attention to his experiments (this vol., i, 58) in which he has shown that in the transformation of benzopinacone, the group in the nucleus does not change its position and that therefore the rearrangement does not take place through a ring formation. E. G.

Solubilities of Certain Organic Acids in Water at Various Temperatures. J. H. Doliński (*Ber.*, 1905, **38**, 1835—1837).—Solubility tables and curves are given for picric, sulphanilic, naphthionic, and α-naphthylamine-2-sulphonic acids in water at temperatures from 0° to 100°. The solubilities of picric and sulphanilic acids correspond very closely and are expressed by the formulæ $0·67 + 0·013t + 0·000195t^2 + 0·0000028t^3$ and $0·64 + 0·0152t + 0·00041t^2$ respectively. The solubility of naphthionic acid is very small, being given by $0·027 + 0·00024t - 0·00000255t^2 + 0·000000205t^3$, whilst α-naphthylamine-o-sulphonic acid is from 10 to 14 times as soluble. T. H. P.

Benzhydroxamic and Dibenzhydroxamic Acids. R. Marquis (*Compt. rend.*, 1905, **140**, 1398—1400).—If a cold solution of benzhydroxamic acid, to which potassium cyanide has been added, is left for several hours and is then acidified with acetic acid, crystals of dibenzhydroxamic acid separate. The reaction is represented by the equation OH·CPh:NOH + KCN = OH·CPh:NOBz + HCN,NH_2·OH.

The yield of dibenzhydroxamic acid depends on the temperature, the concentration, and the quantity of the cyanide in solution, but never exceeded 50 per cent. in the author's experiments. On addition of potassium cyanide to a warm solution of benzhydroxamic acid, diphenylcarbamide and benzoic acid are formed.

Dibenzhydroxamic acid is also formed in small quantity when a solution of benzhydroxamic acid is treated with sodium nitrite, but the chief product is in this case benzoic acid. It is also obtained in 50 per cent. yield when benzhydroxamic acid is heated on the water-bath for several hours with ethyl acetoacetate. The author notes that the observed changes are rather remarkable in view of the great stability of benzhydroxamic acid towards many reagents, for example, strong sulphuric acid. H. M. D.

Elimination of Carbon Dioxide and Carbon Monoxide from α-Phenoxycinnamic Acids. Richard Stoermer and Theodor Biesenbach (*Ber.*, 1905, **38**, 1958—1969).—When α-phenoxycinnamic

acid is heated at 260°, ω-phenoxystyrene is formed, whilst carbon dioxide and carbon monoxide are evolved (compare Stoermer and Kippe, Abstr., 1904, i, 182). Owing to the elimination of carbon monoxide, phenyl phenylacetate is also produced as follows:

$$CHPh{:}C(OPh){\cdot}CO_2H - CO = CHPh{:}C(OPh){\cdot}OH = CH_2Ph{\cdot}CO_2Ph.$$

Phenyl phenylacetate, prepared by the Schotten-Baumann reaction from phenylacetyl chloride and phenol, crystallises in needles and melts at 42°. Since its boiling point, 158° under 7 mm. pressure, is identical with that of phenoxystyrene, it could not be separated from the latter as a product of the action of heat on α-phenoxycinnamic acid, but it was identified by the formation of phenol and phenylacetic acid from it.

Phenoxystyrene boils at 157—158° under 7 mm. pressure. When heated under pressure with alcoholic potassium hydroxide, phenol is formed in quantitative amount, but phenylacetic acid was not detected. By the reducing action of the alcoholic potassium hydroxide, the phenylacetaldehyde formed was reduced to the corresponding alcohol, which was then transformed into styrene. The main product of the action was phenyl vinyl ether.

Phenylacetaldehyde is formed when phenoxystyrene is heated with dilute sulphuric acid.

Ethylbenzene is formed when phenoxystyrene is reduced by sodium and alcohol.

Phenoxystyrene dibromide, $C_{14}H_{12}OBr_2$, prepared by the action of bromine on phenoxystyrene, melts at 91° and gradually undergoes decomposition into the more stable *phenoxystyrene bromide*, $C_{14}H_{11}OBr$, which boils at 156° under 10 mm. pressure and separates from alcohol in needles melting at 60°.

When phenylacetaldehyde is heated under pressure with alcoholic potassium hydroxide at 190°, it forms a mixture of 1 : 3 : 5-triphenylbenzene and another hydrocarbon, probably 1 : 3-diphenyltetramethylene.

α-*p*-Tolyloxycinnamic acid, $CHPh{:}C(O{\cdot}C_6H_4Me)CO_2H$, prepared by the condensation of ethyl *p*-tolyloxyacetate with benzaldehyde by means of sodium (compare this vol., i, 526), melts at 166°. Oglialoro (Abstr., 1890, 320) gives 159—160°.

α-p-*Tolyloxy-β-phenylhydracrylic acid*,

$$OH{\cdot}CHPh{\cdot}CH(O{\cdot}C_6H_4Me){\cdot}CO_2H,$$

separates from water in silky needles and melts at 122°.

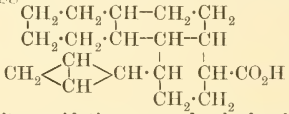
When α-*p*-tolyloxycinnamic acid was heated at 260—270°, carbon dioxide and carbon monoxide were evolved, whilst the formation of an ester of phenylacetic acid was detected. *p*-Tolyloxystyrene was formed together with a crystalline isomeride which is neither an ester nor a ketone. A. McK.

Constitution of Abietic Acid. Hermann Endemann (*Amer. Chem. J.*, 1905, **33**, 523—534).—When abietic acid is heated with acetic anhydride at 160° in a sealed tube, an oily *monoacetyl* derivative is obtained, whence it is concluded that the acid contains one carboxyl group, but does not contain two hydroxyl groups, as stated by Tschirch and Studer (Abstr., 1904, i, 80).

By the oxidation of abietic acid with permanganic acid in acid solution, two acids, $C_{16}H_{24}O_3$ and $C_{16}H_{24}O_4$, are produced together with malonic acid, acrylic acid, and other substances, including an aromatic, neutral substance and certain syrupy acids which have not yet been identified. The *acid*, $C_{16}H_{24}O_4$, separates from an aqueous solution in small crystals and is soluble in chloroform or acetone, sparingly so in benzene, and insoluble in light petroleum. This acid crystallises with $1H_2O$ and melts at 80°; after the removal of the water of crystallisation, it melts at 111—113°; it is dibasic and yields an oily *diacetyl* derivative. The *lead* and *barium* salts are described.

The *acid*, $C_{16}H_{24}O_3$, differs from the foregoing acid in containing an aldehyde group in place of one of the carboxyl groups. It yields the usual reactions for aldehydes, is soluble in benzene, sparingly so in water, separates from an acetone solution as a crystalline mass, and melts at 188°. The *barium* and *lead* salts were prepared.

On the assumption that abietic acid is a retene derivative (compare Abstr., 1904, i, 80, and Easterfield and Bagley, Trans., 1904, **85**, 1238), it is suggested that its constitution may be best represented by the formula



, and that the acids obtained by its oxidation are decahydrophenanthrenalcarboxylic acid, $C_{16}H_{24}O_3$, and decahydrophenanthrenedicarboxylic acid, $C_{16}H_{24}O_4$. It being possible that abietic acid is not so closely related to phenanthrene as is indicated by this formula and that open chains may be present, an attempt was made to ascertain if a double linking exists between two of the carbon atoms. For this purpose, a solution of the dicarboxylic acid, $C_{16}H_{24}O_4$, in chloroform was treated with excess of bromine; the results showed that whilst two atoms of bromine combined with the acid, 4 mols. of hydrogen bromide were produced, indicating that not only had substitution occurred, but that the group $-CH_2 \cdot CH_2-$ had become converted into the group $-CBr{:}CBr-$. E. G.

β-Phenyl-β-ethylethylenelactic [β-Hydroxy-β-phenylvaleric] Acid. PAUL MICHNOWITSCH (*J. pr. Chem.*, 1905, [ii], **71**, 427—430).—*β-Hydroxy-β-phenylvaleric acid*, $OH \cdot CEtPh \cdot CH_2 \cdot CO_2H$, formed along with the trihydric alcohol by the action of potassium permanganate on phenylethylallylcarbinol (Bogorodsky and Ljubarsky, Abstr., 1898, i, 303), crystallises in glistening leaflets, melts at 118—121°, and is easily soluble in alcohol or ether. The *barium*, *calcium*, and *silver* salts are described. G. Y.

Condensation of Benzaldehyde and Ethyl Phenoxyacetate. Claisen's Cinnamic Acid Synthesis by means of Sodium. RICHARD STOERMER and OTTO KIPPE (*Ber.*, 1905, **38**, 1953—1958).—Claisen assumes that his cinnamic acid synthesis from benzaldehyde and ethyl acetate proceeds with the intermediate formation of ethyl phenyl-β-lactate, thus;

$$CHPhO + Na + CH_3 \cdot CO_2Et = ONa \cdot CHPh \cdot CH_2 \cdot COEt + H,$$

a view which is combated by Michael. The experience of the authors on the condensation of benzaldehyde with ethyl phenoxyacetate accords with Claisen's interpretation, since they have isolated α-phenoxy-β-phenylhydracrylic acid as the intermediate product. According to Claisen, sodium hydroxide is not formed from the compound

$$ONa\cdot CHPh\cdot CH_2\cdot CO_2Et$$

during the condensation, since he detected no products of the hydrolysis of ethyl cinnamate. The authors find, however, that when the product resulting from the condensation of benzaldehyde and ethyl phenoxyacetate by means of sodium is decomposed by the calculated amount of glacial acetic acid and water then added, the sparingly soluble sodium α-phenoxy-β-phenylhydracrylate separates, whilst only a small amount of the corresponding ester remains in the ether present together with the ethyl α-phenoxycinnamate, which has not undergone hydrolysis.

Aniline α-phenoxycinnamate, $C_{21}H_{19}O_3N$, prepared by the addition of aniline to an ethereal solution of α-phenoxycinnamic acid, crystallises in needles and melts at 135—136°.

Sodium α-phenoxy-β-phenylhydracrylate,

$$OH\cdot CHPh\cdot CH(OPh)\cdot CO_2Na,5H_2O,$$

is sparingly soluble in cold water and decomposes at about 340° into benzaldehyde and phenoxyacetic acid. The *acid* is precipitated by the addition of mineral acid to the sodium salt as an oil, which, when crystallised from a mixture of benzene and light petroleum, melts at 93—94°. The *acetyl* derivative, formed by heating the acid with acetyl chloride, separates from dilute alcohol in glistening needles and melts at 149°; when acetic anhydride is used, phenoxycinnamic acid is formed. The *aniline* salt separates from benzene in silvery leaflets and melts at 162°. A. McK.

Products of the Condensation of *o*-Aldehydocarboxylic Acids. GUIDO GOLDSCHMIEDT (*Arch. Pharm.*, 1905, **243**, 296—299).—The conclusions of Gadamer (this vol., i, 368; Bruns, *ibid.*, 353) have been anticipated to a large extent by the author and his students (compare especially Fulda, Abstr., 1900, i, 36). C. F. B.

Synthesis of Aromatic β-Ketonic Esters. FÉLIX MARGUERY (*Bull. Soc. chim.*, 1905, [iii], **33**, 548—551).—These esters have been prepared by the application of Friedel and Craft's reaction to the chlorides of the monoethyl esters of the malonic acid series (this vol., i, 507) and aromatic hydrocarbons (compare Bouveault, Abstr., 1896, i, 551, 616, and 1897, i, 530).

Ethyl p-*toluoylacetate*, $C_6H_4Me\cdot CO\cdot CH_2\cdot CO_2Et$, is a colourless, pleasant-smelling, slightly oily liquid boiling at 170° under 30 mm. pressure; it is soluble in alcohol or benzene and insoluble in water, and gives an intensely violet coloration with alcoholic ferric chloride. The *copper* derivative forms green crystals and is soluble in chloroform. With hydrazine, the ester furnishes 3-tolylpyrazolone melting at 123°.

p-*Toluoylacetic acid*, obtained by hydrolysing the ester by Córésole's method, forms micaceous scales and melts and decomposes at 96°,

yielding carbon dioxide and a ketone which distils at 220°, and on oxidation furnishes terephthalic acid.

Ethyl 1 : 4-*dimethylbenzoylacetate*, $C_6H_3Me_2\cdot CO\cdot CH_2\cdot CO_2Et$, is an oily, slightly rose-coloured liquid, which boils at 176—180° under 14 mm. pressure and gives an intense red coloration with ferric chloride and yields a crystalline *copper* derivative.

Ethyl 1 : 4-*dimethylbenzoylpropionate* resembles the foregoing ester, boils at 190—195° under 18 mm. pressure, has a sp. gr. 1·038 at 19°/19°, n_D 1·50623 at 19°, and gives a bluish-violet coloration with ferric chloride. When hydrolysed by boiling with aqueous potassium hydroxide, it yields *p*-xylyl ethyl ketone boiling at 238—240°.

T. A. H.

Hydrazine Derivatives of Tetrachlorophthalic Acid. Isaac K. Phelps (*Amer. Chem. J.*, 1905, **33**, 586—590).—When ethyl tetrachlorophthalate (1 mol.) is heated with hydrazine hydrate (1 mol.) in presence of ether for 10 hours at 100° in a sealed tube, the *hydrazine* compound of the primary hydrazide,

$$C_6Cl_4(CO\cdot NH\cdot NH_2)_2,N_2H_4,$$

separates; it forms yellow crystals, is insoluble in ether, and sparingly so in hot alcohol, and when heated does not melt, but becomes charred at 290—300°. If this compound is boiled with a hot alcoholic solution of hydrogen chloride, the *primary hydrazide*, $C_6Cl_4(CO\cdot NH\cdot NH_2)_2$, is obtained as a colourless substance which is insoluble in the ordinary organic solvents.

The *secondary hydrazide*, $C_6Cl_4{<}\begin{matrix}CO\cdot NH\\ |\\ CO\cdot NH\end{matrix}$, obtained by heating tetrachlorophthalic acid (1 mol.) with hydrazine hydrate (1·5 mols.) at 140—150° for half an hour under a reflux condenser, separates from glacial acetic acid in pale yellow crystals, melts and decomposes slightly at 286—287°, is insoluble in most organic solvents, and is soluble in aqueous alkali hydroxides and reprecipitated by acids; its *diacetyl* derivative melts at 203—204°; its *mono-sodium*, *mono-potassium*, and *mono-silver* salts were prepared and analysed. By the action of ethyl chlorocarbonate on the silver salt, the *compound* $C_6Cl_4{<}\begin{matrix}CO\cdot NH\\ |\\ CO\cdot N\cdot CO_2Et\end{matrix}$ is obtained, which forms white, prismatic crystals and melts at 244—245°.

No evidence was obtained in these experiments of any reaction between the hydrazine and the chlorine in the benzene nucleus.

E. G.

Synthesis of Aromatic Substituted Homosuccinic Acids by means of Paraconic Acids. Johan F. Eijkman (*Chem. Centr.*, 1905, i, 1388; from *Chem. Weekblad*, **2**, 229—231).—Aromatic hydrocarbons may be condensed with lactone-carboxylic acids by allowing the mixture to remain in presence of aluminium chloride for several days.

Diphenylmethylsuccinic acid, $CHPh_2\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$, prepared from phenylparaconic acid and benzene, crystallises in needles, is

readily soluble in alcohol, less so in hot water or benzene, and sparingly so in cold water; it melts at 175°, giving off vapour and probably forming an anhydride.

Phenyltolylmethylsuccinic acid,

$$C_6H_4Me\cdot CHPh\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H,$$

obtained from phenylparaconic acid and toluene, crystallises from dilute alcohol in needles and melts at 150—153°, forming an anhydride.

Phenylethylphenylmethylsuccinic acid,

$$C_6H_4Et\cdot CHPh\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H,$$

prepared from phenylparaconic acid and ethylbenzene, crystallises from benzene or dilute alcohol in needles and melts and gives off gas at 135—140°. E. W. W.

***iso*Artemisin (δ-Hydroxysantonin).** EDGAR WEDEKIND and A. KOCH (*Ber.*, 1905, **38**, 1845—1851. Compare Jaffé, Abstr., 1897, i, 628; Bertolo, Abstr., 1901, i, 718; Freund and Mai, Abstr., 1902, i, 101; Horst, Abstr., 1902, i, 387).—Chlorosantonin, $C_{15}H_{17}O_3Cl,H_2O$ (this vol., i, 212), has $[\alpha]_D$ −54·75°, is only slightly soluble in water, light petroleum, or ether, but easily so in other organic solvents, and dissolves slowly in warm aqueous sodium hydroxide. It dissolves in cold concentrated sulphuric or nitric acids, and is decomposed when warmed with the former. *δ-Hydroxysantonin*, $C_{15}H_{18}O_4$, is formed when chlorosantonin is heated with 1 mol. of potassium hydroxide in alcoholic solution at 100° or with excess of aqueous sodium acetate in a sealed tube at 110—115°. It crystallises in colourless needles, melts at 214—215°, has $[\alpha]_D$ −108·62°, and dissolves readily in hot alcohol, acetone, or chloroform. It is insoluble in boiling aqueous sodium hydroxide, but dissolves in cold concentrated sulphuric or nitric acids and in hot hydrochloric acid to a yellow solution, which, on dilution, deposits a yellow *product* melting at 150—155°. The *phenylhydrazone*, $C_{15}H_{18}O_3{:}N\cdot NHPh$, crystallises in yellow, microscopic needles, melts and decomposes at 176—178°, and dissolves in concentrated sulphuric acid to a green solution, and in fuming hydrochloric acid to a yellow solution which becomes greenish-yellow and deposits a precipitate.

G. Y.

Ethyl Phthalylacetoacetate. CARL BÜLOW [and, in part, E. SIEBERT] (*Ber.*, 1905, **38**, 1906—1917. Compare E. Fischer and Koch, Abstr., 1883, 806; Bülow, *ibid.*, 1887, 144).—The phenylhydrazone of ethyl phthalylacetoacetate is not decomposed when heated with concentrated sulphuric acid at 175° or when boiled with acetic acid or anhydride. Aqueous baryta or 30 per cent. potassium hydroxide solution hydrolyses the ester to the corresponding *acid*, $C_{18}H_{14}O_4N_2$; this crystallises from hot water in small, compact prisms, melts and decomposes at 233—234°, and is readily soluble in alcohol, acetone, or acetic acid. A solution of the ammonium salt yields precipitates with solutions of the salts of most heavy metals. The *hydrazone* of ethyl phthalylacetoacetate, $C_{14}H_{14}O_4N_2$, obtained by the action of hydrazine hydrate on an acetic acid solution of ethyl phthalylacetoacetate, crystallises from acetic acid in small, colourless needles, melts at 290°, and is readily soluble in most organic solvents.

Ethyl phthaloxime-acetoacetate oxime,

$$NOH:CMe\cdot C(CO_2Et):C<\substack{N(OH)\\ C_6H_4-}>CO,$$

obtained by the action of hydroxylamine hydrochloride on an acetic acid solution of the ester at the ordinary temperature, melts at 224° and is soluble in cold alkalis but insoluble in water.

3-*Methyl*-4-*phthalyl*-5-iso*oxazolone*, $CO<\substack{-O-\\ C_6H_4}>C:C<\substack{CMe:N\\ CO-O}$, obtained by the action of hydroxylamine hydrochloride on the ester according to Schiff's method, crystallises from acetic acid in colourless needles melting at 203°, and is insoluble in alkalis, but dissolves readily in most organic solvents.

Semicarbazide and ethyl phthalylacetoacetate in alcoholic solution yield the sparingly soluble semicarbazone of *ethyl phthalylsemicarbazone-acetoacetate semicarbazone*, $C_{36}H_{18}O_5N_6$(?), which decomposes and melts at 243° and then solidifies and melts again above 280°. The filtrate from the disemicarbazone yields *ethyl phthalylacetoacetate semicarbazone*, $C_{15}H_{15}O_5N_3$, in the form of long needles melting at 188—189°, and readily soluble in alcohol, acetone, or chloroform.

Hydrazine hydrate reacts with ethyl *o*-carboxybenzylacetoacetate (Abstr., 1887, 144), yielding 4-o-*carboxybenzyl*-3-*methyl*-5-*pyrazolone*, $C_{12}H_{12}O_3N_2$, which crystallises in colourless needles melting at 254°. It is both basic and acidic in character. Hydroxylamine transforms the same ester into 4-o-*carboxybenzyl*-3-*methyl*-5-iso*oxazolone*, $C_{12}H_{11}O_4N$, which crystallises in needles, dissolves in alcohol, acetone, acetic acid, or alkalis, and melts at 173°.

Semicarbazide and the ester yield 4-o-*carboxybenzyl*-3-*methyl*-5-*pyrazolone*-1-*carboxylamide*, $C_{13}H_{13}O_4N_3$, which melts and decomposes at 181° and then solidifies and melts again above 200°. The readiness with which the ester of *o*-carboxybenzylacetoacetic acid forms ring compounds with hydrazine, hydroxylamine, &c., is attributed to the labile H atom, $CO_2H\cdot C_6H_4\cdot CH_2\cdot CHAc\cdot CO_2Et$, which is not present in ethyl phthalylacetoacetate. J. J. S.

Indophenol Derivatives from *p*-Chlorophenol. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 158091).—When *p*-chlorophenol is mixed with a molecular quantity of an alkylated *p*-diamine or *p*-aminophenol and oxidised, compounds are obtained having the composition of *o*-indophenols, $O:C_6H_3Cl:N\cdot C_6H_4X$, where $X = OH$ or $NAlk_2$. Thus alkaline potassium ferricyanide oxidises a mixture of *p*-chlorophenol and dimethyl-*p*-phenylenediamine to an *indophenol* which dissolves in alcohol to a blue solution, becoming red on addition of acids. Sodium sulphide reduces it to the *leuco*-compound which forms colourless crystals becoming blue in air. A blue dye is obtained on fusing the indophenol or its leuco-compound with sodium sulphide and sulphur.

The *indophenol* from *p*-chlorophenol and *p*-aminophenol forms a green, crystalline *sodium* salt, dissolving in water, alcohol, or concentrated sulphuric acid to blue solutions. Similar compounds are obtained from *p*-chlorophenol and *p*-amino-*o*-cresol or 2 : 6-dichloro-4-amino-

phenol. It is not possible to replace the *p*-chlorophenol in this reaction by *p*-cresol or phenol-*p*-sulphonic acid. C. H. D.

Iodo-hydriodo-compounds of Non-nitrogenous Derivatives of Anthraquinone. CARL LIEBERMANN and LEONHARD MAMLOCK (*Ber.*, 1905, 38, 1784—1796. Compare Abstr., 1904, i, 901).—On passing hydrogen iodide into a cold saturated solution of anthraquinone in benzene, small, dark, lustrous leaflets of a *compound*, $2C_{14}H_{10}O,2HI,I_2$, derived from anthranol, separate; the compound probably has the constitution $2C_6H_4<\begin{matrix}CHI\text{——}\\CI(OH)\end{matrix}>C_6H_4,I_2$, and the mechanism of its formation is discussed in detail. On mixing molecular proportions of carbon disulphide solutions of anthranol and iodine, a *compound*, $C_{14}H_{10}O,HI,I_2$, crystallising in dark needles, is formed. In benzene solution, anthranol and hydrogen iodide give a *substance* of approximately the composition $4C_{14}H_{10}O_4,HI,I_2$. On further addition of hydrogen iodide, green crystals of $4C_{14}H_{10}O,4HI,I_2$ are obtained. In all cases, the compounds formed give varying analytical data, owing to the readiness with which they lose a portion of their iodine.

On passing hydrogen iodide into a solution of 2-methylanthraquinone in benzene, the crystalline *compound*, $C_{15}H_{12}O,HI,I_2$, derived from β-methylanthranol, is obtained; on decomposition with alcohol, it gives 2-methylanthranol, which melts at 80—84° and not at 100°, as stated by Limpricht (Abstr., 1901, i, 145). 2-Methylanthranol combines with iodine and hydrogen iodide in benzene solution to form a *compound*, $2C_{15}H_{12}O,2HI,I_3$; with iodine alone in benzene solution, the product has the composition $2C_{15}H_{11}O,2HI,I_2$.

With hydrogen iodide in benzene solution, phenylanthranol gives a *compound*, $2C_{20}H_{14}O,2HI,I_3$, identical with the substance obtained by a similar method from phenyloxanthranol (Liebermann, Glawe and Lindenbaum, *loc. cit.*). 1-Hydroxyanthraquinone, under similar conditions, gives the *compound* $C_{14}H_{10}O_2,HI,I_3$, which is decomposed by alcohol and sulphur dioxide giving *1-hydroxy-9-anthranol*; this substance is better prepared by reducing 1-hydroxyanthraquinone with tin and hydrochloric acid in presence of acetic acid, and crystallises from glacial acetic acid in bright yellow needles melting at 136—138°.

The constitution of these iodo-derivatives is dealt with in detail. W. A. D.

Anthragallolamide [2-Amino-1 : 3-dihydroxyanthraquinone]. FRIEDRICH BÖCK (*Monatsh.*, 1905, 26, 571—593. Compare Georgievics, Abstr., 1886, 69).—Anthragallolamide is formed by the action of ammonium chloride on anthragallol in dilute alkali hydroxide solution, or in large quantities by exposing finely powdered anthragallol, dried at 150°, to the action of ammonia vapour for several days and heating the ammonium salt so formed at 130°; the *barium* salt, $C_{14}H_7O_4NBa$, was analysed. The *diazo-anhydride*, $C_8H_4O_2<\begin{matrix}C(OH):C\cdot N_2\\CH\text{===}C\cdot O\end{matrix}$, is formed by the action of amyl nitrite on the amine in slightly acid alcoholic solution; it crystallises in glistening, yellow, microscopic plates, detonates when rapidly heated, is slightly soluble in water, but easily

so in aqueous alkali hydroxides to red solutions, and when reduced by stannous chloride in alkaline solution yields purpuroxanthin, which melts at 270° (m. p. 263°, Plath, *Ber.*, 1877, **10**, 615). This, when heated with methyl iodide and aqueous potassium hydroxide at 120°, forms the dimethyl ether which melts at 187° (m. p. 180°, Plath, *loc. cit.*) and dissolves in hot aqueous alkali hydroxide to a red solution, which deposits a red, flocculent precipitate on cooling. In one experiment, persistent methylation led to the formation of a *product*, $C_{14}H_5O_2Me(OMe)_2$, which melted at 153° and was not acted on by hot aqueous alkali hydroxides. When boiled with benzaldehyde, anthragallolamide forms a *benzylidene* derivative, $C_{14}H_7O_4N{:}CHPh$, which crystallises in glistening, brown prisms, melts at 257—258°, and is easily hydrolysed by dilute alkali hydroxides or acids or by warm pyridine; when shaken with acetic anhydride and pyridine, it forms an *acetyl* derivative as a yellow, crystalline mass, which melts at 158° and is hydrolysed by boiling alcohol. When heated with aqueous or alcoholic ammonia under pressure at 100°, anthragallol dimethyl ether (m. p. 160°, Abstr., 1903, i, 266) forms an *amino-product* which crystallises in slender, violet needles and melts at 231°. It forms a *hydrochloride* which crystallises in red needles, and when warmed yields ammonium chloride and anthragallol dimethyl ether, which is formed also by warming the amino-compound with aqueous potassium hydroxide.

G. Y.

1 : 2 : 5-Trihydroxyanthraquinone. FARBENFABRIKEN VORM FRIEDR. BAYER & Co. (D.R.-P. 156960).—When alizarin is dissolved in fuming sulphuric acid (30 per cent. SO_3) to which boric acid has been added, and agitated at 30—35° until a violet solution is obtained, a sulphuric ester of 1 : 2 : 5-trihydroxyanthraquinone is formed. The product is decomposed by water, and after purification and crystallisation from acetic acid yields red needles of 1 : 2 : 5-*trihydroxyanthraquinone* melting at 273—274°. The *triacetyl* derivative melts at 227—228°.

C. H. D.

Methylnataloe-emodin and Nataloe-emodin. EUGÈNE LÉGER (*Compt. rend.*, 1905, **140**, 1464—1466. Compare Abstr., 1902, i, 549, 685; 1903, i, 356).—Methylnataloe-emodin,

$$OH\cdot C_6H_3<^{CO}_{CO}>C_6HMe(OH)\cdot OMe,$$

yields 4-hydroxy*iso*phthalic acid melting at 293° (corr.) on fusion with potassium hydroxide, is oxidised to oxalic acid by fuming nitric acid, and on treatment with bromine yields a *pentabromide*, $C_{16}H_7O_5Br_5$, which crystallises in dark red needles, melts at 293—295° (corr.), and is soluble in acetic acid or toluene and sparingly so in methyl alcohol. *Diacetylmethylnataloe-emodin*,

$$OAc\cdot C_6H_3<^{CO}_{CO}>C_6HMe(OMe)\cdot OAc,$$

forms long, brilliant, needle-shaped crystals, melts at 169° (corr.), and is soluble in alcohol or chloroform, sparingly so in ether, and insoluble in water. Nataloe-emodin (trihydroxymethylanthraquinone), obtained from methylnataloe-emodin by the action of concentrated hydrochloric

acid, melts at 214·5° (corr.) and not at 220·5° as previously stated (Abstr., 1902, i, 549 ; 1903, i, 356) ; *triacetylnataloe-emodin*,

$$OAc\cdot C_6H_3<{}^{CO}_{CO}>C_6HMe(OAc)_2,$$

crystallises from methyl alcohol in long, bright yellow needles melting at 203·7° (corr.). M. A. W.

Menthones and Menthols obtained by the Catalytic Reduction of Pulegone with Metallic Nickel. Albin Haller and Camille Martine (*Compt. rend.*, 1905, **140**, 1298—1303. Compare this vol., i, 220).—By the action of nickel sponge on pulegone at 140—160°, the authors have obtained a liquid which boils at 94—95° under 16 mm. pressure, is dextrorotatory, has $[\alpha]_D + 5°$ to $+ 8°$, furnishes an oily *oxime* and condenses with benzaldehyde, in presence of hydrogen chloride, forming hydrochlorobenzylidenementhone, identical with that obtained from natural menthone. This liquid is regarded as a mixture of ketones provisionally designated pulegomenthones. By the prolonged action of nickel sponge on pulegone at 150—160°, a mixture of "pulegomenthols" was obtained. The crude product boils at 107—108° under 16 mm. pressure, has the odour of menthol, and is slightly dextrorotatory ($[\alpha]_D + 6°$ to $+ 8°$). When cooled, the mixture partially solidifies, and by fractional crystallisation of the deposited matter from light petroleum, menthol and *α-pulegomenthol* were obtained. α-Pulegomenthol melts at 84—85°, has $[\alpha]_D + 30°$ and $+ 23°10'$ in 4 and 10 per cent. solutions in alcohol respectively ; it may be identical with Beckmann's *iso*menthol (Abstr., 1897, i, 248).

On treatment with phthalic anhydride, the oily product remaining after freezing out menthol and α-pulegomenthol gave a mixture of the following esters : menthyl phthalate, *α-pulegomenthyl hydrogen phthalate* (m. p. 104—105° and $[\alpha]_D + 27·5°$ in 4·724 per cent. solution in alcohol), and *β-pulegomenthyl hydrogen phthalate*, which melts at 137—138° and has $[\alpha]_D + 8·9°$. *β-Pulegomenthol*, regenerated from the acid phthalate, is a syrupy liquid, which does not crystallise when cooled with ice and salt, boils at 212—212·5° (corr.), and has $[\alpha]_D + 2·6°$ at 14°. Carvone, on reduction with nickel sponge, furnishes a mixture of dihydrocarvols, boiling at 216—218° and yielding a *phenylurethane* which melts at 107—108°. Under the same conditions, thujone yields thujol, citronellol gives dihydrocitronellol, and terpineol furnishes hexahydrocymene. T. A. H.

Cyanocamphoracetic, α-Cyanocamphorpropionic, and α-Cyanocamphor*iso*butyric Acids and their Principal Derivatives. Albin Haller and A. Couréménos (*Compt. rend.*, 1905, **140**, 1430—1435).—Sodiocyanocamphor reacts with the halogen-substituted derivatives of the fatty acids to form compounds of the type

$$C_8H_{14}<{}^{C\cdot CN}_{\overset{||}{C}\cdot OR}$$

(compare Abstr., 1891, 1499 ; 1892, 1344 ; 1894, i, 338), and in the case of α-bromopropionic acid, which contains an asymmetric carbon atom, sodiocyanocamphor resolves it into its two optical isomerides,

forming a dextro- and a lævo-derivative. *Ethyl cyanocamphoracetate*, $C_8H_{14}<\begin{array}{l}C\cdot CN\\ \| \\ C\cdot O\cdot CH_2\cdot CO_2Et\end{array}$, prepared from sodiocyanocamphor and ethyl chloroacetate or iodoacetate in xylene solution, is an oily liquid boiling at 190—200° under 15 mm. pressure, has a sp. gr. 1·09 at 0° and $[\alpha]_D + 79·44°$, is insoluble in water or alkaline solutions, soluble in alcohol, chloroform, or benzene, and hydrolysed by hydrochloric acid, yielding cyanocamphor. *Methyl cyanocamphoracetate*,

$$C_8H_{14}<\begin{array}{l}C\cdot CN\\ \| \\ CO\cdot CH_2\cdot CO_2Me\end{array},$$

boils at 150—156° under 25 mm. pressure, melts at 67°, and has $[\alpha]_D + 78·10°$. *Cyanocamphoracetic acid*, $C_8H_{14}<\begin{array}{l}C\cdot CN\\ \| \\ C\cdot O\cdot CH_2\cdot CO_2H\end{array}$, obtained by the action of alcoholic potassium hydroxide on either of the preceding compounds, crystallises from alcohol, xylene, or benzene and chloroform, melts at 98—99°, has $[\alpha]_D + 113·69°$, is insoluble in water, but soluble in ether or light petroleum. The *potassium* salt, $C_{13}H_{16}O_3NK$, forms thin, white needles soluble in water or alcohol; the *copper* salt, $(C_{13}H_{16}O_3N)_2Cu$, is a grey, amorphous powder insoluble in water but soluble in methyl or ethyl alcohol. *Cyanocamphoracetamide*, $C_8H_{14}<\begin{array}{l}C\cdot CN\\ \| \\ C\cdot O\cdot CH_2\cdot CO\cdot NH_2\end{array}$, prepared by the action of alcoholic ammonia in sealed tubes at 100° on ethyl cyanocamphoracetate, crystallises from benzene, melts at 120°, and has $[\alpha]_D + 95·73°$. Ethyl α-bromopropionate reacts with sodiocyanocamphor to form two *ethyl-α-cyanocamphorpropionates*, $C_8H_{14}<\begin{array}{l}C\cdot CN\\ \| \\ C\cdot O\cdot CHMe\cdot CO_2Et\end{array}$, which are enantiomorphously related to one another; the more soluble one melts at 49°, has $[\alpha]_D + 144·08°$, and crystallises from methyl alcohol in beautiful needles; the *lævo*-compound melts at 74·5°, has $[\alpha]_D - 33·78°$, and crystallises in white plates soluble in alcohol, chloroform, or benzene. *Methyl-α-cyanocamphorpropionate*, $C_8H_{14}<\begin{array}{l}C\cdot CN\\ \| \\ C\cdot O\cdot CHMe\cdot CO_2Me\end{array}$, has also been obtained in two forms; the one compound melts at 44° and has $[\alpha]_D + 175·44°$ and the isomeride crystallises in the monoclinic system (Wyrouboff), melts at 80—81°, and has $[\alpha]_D - 41·76°$. By the action of alcoholic potassium hydroxide on the *dextro*-ethyl α-cyanocamphorpropionate, the corresponding *α-cyanocamphorpropionic acid*,

$$C_8H_{14}<\begin{array}{l}C\cdot CN\\ \| \\ C\cdot O\cdot CHMe\cdot CO_2H\end{array},$$

is obtained, which melts at 109°, has $[\alpha]_D + 93·06°$, forms *ammonium*, *silver*, and *copper* salts; the *amide*, $C_8H_{14}<\begin{array}{l}C\cdot CN\\ \| \\ C\cdot O\cdot CHMe\cdot CO\cdot NH_2\end{array}$, crystallises in thin needles, melts at 170·5°, and has $[\alpha]_D + 93·02°$. The *acid*, similarly obtained from *lævo*-ethyl α-cyanocamphorpropionate, melts at 85°, has $[\alpha]_D + 13·43°$, forms an *ammonium*, a *silver*, and a *copper* salt; the *amide* forms beautiful white needles soluble in benzene, ether, light petroleum, or chloroform, melts at 183°, and has

$[\alpha]_D + 75\cdot20°$. *Ethyl cyanocamphorisobutyrate*, $C_8H_{14}<\begin{matrix}C\cdot CN\\ \| \\ C\cdot O\cdot CMe_2\cdot CO_2Et\end{matrix}$, is an oil boiling at 220—226° under 18 mm. pressure. M. A. W.

Transformation of Carvone into α-Phellandrene. CARL D. HARRIES and MANUEL JOHNSON (*Ber.*, 1905, **38**, 1832—1835).—Wallach has shown (Abstr., 1904, i, 1035) that the suitable reduction of active nitrophellandrene yields $\Delta^{5\cdot6}$-menthene-2-one; by converting the latter into α-phellandrene the author now renders it possible to transform carvone into α-phellandrene.

Chlorophellandrene, $CMe<\begin{matrix}CCl:CH\\CH\cdot CH_2\end{matrix}>CHPr^{\beta}$, obtained by the action of phosphorus pentachloride on Δ^6-menthene-2-one, is a colourless, highly refractive oil with a faint ethereal odour, and has $\alpha_D - 28°$ in a decimeter tube at 20°. On reduction with zinc dust in methyl-alcoholic solution and in an atmosphere of nitrogen, it is converted into α-phellandrene.

Δ^6-*Menthene-2-amine*, $CMe<\begin{matrix}CH(NH_2)\cdot CH_2\\CH\text{———}CH_2\end{matrix}>CHPr^{\beta}$, obtained by reducing the oxime of Δ^6-menthene-2-one with zinc dust and acetic acid, is a colourless oil which boils at 89° under 14 mm. pressure, has a basic, camphor-like odour, n_D 1·47957 at 20°, sp. gr. 0·8896 at 20°, and $\alpha_D + 104°40'$ in a decimetre tube at 20°. Its *hydrochloride* melts at 188°. On treating the base with phosphoric acid and distilling the phosphate in a vacuum, a hydrocarbon is obtained which is probably α-phellandrene. T. H. P.

Essential Oil of Achillea Nobilis. P. ECHTERMEIER (*Arch. Pharm.*, 1905, **243**, 238—246).—The oil examined was obtained from *Achillea nobilis* when flowering; it had sp. gr. 0·9353 at 15° and rotation $-20\cdot82°$ in a 200 mm. tube, and boiled at 170—265°, the three fractions collected containing C 84—79 and H 11·4—10·7 per cent.; the ester number corresponded with 18 per cent. of $C_{10}H_7\cdot OAc$, the acetyl number with 13 per cent. of $C_{10}H_7\cdot OH$.

No oxime could be obtained from the oil. When some of it was allowed to fall gradually on to phosphoric oxide, the mixture being cooled, and the product distilled and then redistilled repeatedly over sodium, camphene was obtained together with an *oil* which also had the composition $C_{10}H_{16}$; this oil boiled at 171—177°.

When the crude oil was boiled with alcoholic potassium hydroxide, decoic, acetic, and formic acids seemed to be present among the products. Small quantities of a phenol were also present. Further products were borneol; an *oil* which also had the composition $C_{10}H_{18}O$, boiled at 197—201°, and had an odour resembling that of linalool; and an *oil* which boiled at 248—265°, had the composition $C_{10}H_{16}O$, and yielded, when distilled repeatedly over sodium, camphene and an *oil* which boiled at 240—245° and had the composition $C_{10}H_{16}$, resembling in these respects the less volatile fractions of oil of camomile and of other essential oils. C. F. B.

Ethereal Oils. SCHIMMEL & Co. (*Chem. Centr.*, 1905, i, 1469—1471; from Schimmel's *Geschäftsber.*, April, 1905. Compare Abstr., 1903, i, 185; 1904, i, 603).—Para copaiva balsam yields 62·5 per cent. of a yellow oil, which is soluble in 7·5—8 volumes of 95 per cent. alcohol and has a sp. gr. 0·9180 at 15°, $\alpha_D - 78°48'$, n_D 1·50096 at 20°, acid number 3·14, and ester number 0. From Bahia and Angostura copaiva balsams, 61·93 and 52·3 per cent. respectively of slightly yellow oils are obtained. The former has a sp. gr. 0·8982 at 15°, $\alpha_D - 9°37'$, n_D 1·49460, acid number 7·87, and saponification number 9·82; it dissolves in 8—10 volumes of 95 per cent. alcohol, forming a slightly turbid solution. The Angostura oil is soluble in 5·5 volumes of 95 per cent. alcohol; it has a sp. gr. 0·9161 at 15°, $\alpha_D - 2°20'$, n_D 1·50169 at 20°, acid number 10·89, and ester number 0.

Cypress oil distilled from fresh material in the South of France is soluble in 5—6 volumes of 90 per cent. alcohol; it has a sp. gr. 0·868—0·878 at 15°, $\alpha_D + 22°$ to $+31°$, acid number 0, and ester number 5—10. The acetyl derivative has ester number 10—15. The oil distilled in Germany dissolves in 2—6 volumes or more of 90 per cent. alcohol; it has a sp. gr. 0·88—0·892 at 15°, $\alpha_D + 4°$ to $+18°$, acid number 1·5—3, and ester number 15—22 (acetyl derivative 43—49). The oil obtained from the fruit is similar to the ordinary French oil, and is soluble in 6 volumes or more of 90 per cent. alcohol; it has a sp. gr. 0·8686 at 15°, $\alpha_D + 30°48'$, acid number 0, and ester number 6·74 (acetyl derivative 11·78).

Bergamot oil is chiefly adulterated with lemon oil or the terpenes of lemon oil; the addition of these substances is indicated by the increased rotatory power of the oil.

The bright yellow oil from *Eucalyptus polybractea* closely resembles that of *Eucalyptus odorata*, and contains a considerable quantity of cineol; it has a sp. gr. 0·9193 at 15° and $\alpha_D - 1°3'$, and smells strongly of cuminaldehyde.

Further examination of ginger grass oil has shown that it cannot be an inferior Palma rose oil, but is probably derived from a plant which closely resembles *Andropogon Schoenanthus*. The dihydrocuminol, $C_{10}H_{16}O$ (*Geschäftsber.*, October, 1904; Walbaum and Hüthig, Abstr, 1905, i, 53), obtained from this oil, when reduced with sodium amalgam, yields a tetrahydrocuminol, $C_{10}H_{18}O$, which boils at 216—218° or at 79—80° under 5 mm. pressure and has a sp. gr. 0·9419 at 15°; the phenylurethane compound melts at 85—86°. When oxidised with potassium dichromate and sulphuric acid, it forms *dihydrocuminaldehyde*, $C_{10}H_{14}O$, and dihydrocuminic acid. The former boils at 235° under 755 or at 85° under 4 mm. pressure; it has a sp. gr. 0·9698 at 15°, $\alpha_D - 37°54'$, and n_D 1·50702 at 20°. The semioxamozone melts at 228°. *Dihydrocuminic acid*, $C_{10}H_{14}O_2$, melts at 130—131° and yields a *dibromide* and a *hydrobromide* which melt at 167—168° and 175° respectively; it is not identical with the acid obtained by Villiger and von Baeyer from nopinic acid. When cautiously heated with nitric acid, it forms cuminic acid, but when added to cold concentrated nitric acid it yields 3-nitrocuminic acid.

Inactive carvone has been found in ginger grass oil and methyl-

heptenone in Palma rose oil. A sample of hop oil was found to be adulterated with Gurjun balsam oil. The hydrochloride of *iso*safrole, prepared by passing dry hydrogen chloride into *iso*safrole, contains 1 mol. HCl and reacts with sodium methoxide, ethoxide, or amyloxide. The *methoxy*-compound boils at 110—112° under 5 mm. pressure and has a sp. gr. 1·1116 at 15° and n_D 1·51619 at 15°. The *ethoxy*-compound boils at 110—111° under 3·5 mm. pressure, and has a sp. gr. 1·0796 at 15° and n_D 1·50884 at 15°. The *amyloxy*-compound boils at 136—137° under 13·5 mm. pressure, and has a sp. gr. 1·0258 at 15° and n_D 1·49775 at 15°. By the action of water at a high temperature, or of dilute acids on these compounds, the alcohol appears to be regenerated, but strong alkalis have no action. By the action of phosphorus pentachloride on the methoxy-compound and treatment of the product with water, a compound, $C_{10}H_8O_3$, is formed, which is possibly the 1 : 3 : 4-allylcatechol ester of carbonic acid; it has an odour slightly resembling that of coumarin, melts at 84·5—85°, and boils at 130—135° under 3·5 mm. pressure. When treated with acetic acid according to Bertram's method, combination does not take place at the double linking, but a substance is formed which is probably a polymeric *iso*safrole; it melts at 90—91° and boils at 220° under 3 mm. pressure. *iso*Safrole itself reacts with phosphorus pentachloride, forming a product which, when boiled with a strong solution of potassium hydroxide in alcohol, yields the ketone, $CH_2O_2{:}C_6H_3{\cdot}COEt$, melting at 39°.

Small quantities of a base which has a narcotic odour have been found in oil of caraway, together with dihydrocarvone and dihydrocarveol. The base boiling at 135—140° under 3—4 mm. pressure, which was found in patchouli oil (Abstr., 1904, i, 604), forms a *hydrochloride*, $C_{14}H_{23}ON,HCl$, which melts at 147·5—148·5°; the *platinichloride* melts at 175°.

The oil from the wood of *Fagara octandra*, a Mexican *Rutaceae*, is bright yellow and has an odour which resembles that of linalool; it has a sp. gr. 0·922 at 15°, $\alpha_D + 2°30'$, and ester number 6·09. *Inula graveolens* yields a brown oil, which has a green fluorescence and probably contains bornyl acetate; it has a sp. gr. 0·9754 at 15°, $\alpha_D - 36°40'$, acid number 8·45, and ester number 161·3 (acetyl derivative 239·38). The oil prepared from the leaves of *Cupressus Lambertiana* is yellowish-green and has an odour similar to that of balm; it has a sp. gr. 0·8656 at 15°, $\alpha_D + 31°53'$, acid number 1·5, and ester number 13·9 (acetyl derivative 50·82). The leaves of *Laurus Camphora*, distilled in Cannes, yielded about 0·52 per cent. of a colourless oil, which has an odour similar to that of cardamom. Pinene, cineol, *l*-terpineol, and probably camphene are contained in this oil; it has a sp. gr. 0·9058 at 15°, $\alpha_D - 26°12'$, acid number 0·34, and ester number 8·82 (acetyl derivative 46·9). About 0·76 per cent. of a brownish-yellow oil was distilled from the fruit of *Amomum mala* in Amani (German E. Africa); it contains a considerable quantity of cineol, together with terpineol, and has a sp. gr. 0·9016 at 15°, $\alpha_D - 10°46'$, acid number 3·5, and ester number 1·7 (acetyl derivative 67·05). Vetiver oil, prepared from the fresh roots, is bright brown, and has a sp. gr. 1·0023 at 15°, $\alpha_D + 33°42'$, acid number 16·06, and ester number

12·16 (acetyl derivative 142·35). The balsam of *Hardwickia binata* (oil of Ennaikulavo), when distilled with steam, yields about 44 per cent. of a colourless, rather limpid oil, which has a sp. gr. 0·9062 at 15°, a_D $-7°42'$, acid number 0·85, and ester number 2·88. Bay berries from the Bermudas yield 3·66 per cent. of a yellowish-brown oil, which has a sp. gr. 1·0170 at 15° and a_D $-7°3'$; it contains 73 per cent. of phenols. Eugenol and *l*-phellandrene were isolated, but probably not myrcene. About 0·29 per cent. of a lemon-yellow oil may be obtained from *Artemisia annua*; it has a sp. gr. 0·8912 at 15°, a_D $-1°18'$, acid number 3·8, and ester number 19·2 (acetyl derivative 44·5). The bark of *Tetranthera polyantha var. citrata* yields 0·81 per cent. of a lemon-yellow oil, which probably contains citral and citronellal, and has a sp. gr. 0·8904 at 15° and a_D $+10°11'$, whilst from the leaves 5·42 per cent. of a bright yellow oil is obtained, which contains citral and cineol and has a sp. gr. 0·9042 at 15° and a_D 15°41'.

The quantitative determination of aldehydes and ketones by means of a saturated solution of sodium sulphite gives very good results for carvone and pulegone, and is also satisfactory for citral and cinnamaldehyde, but not for citronellal. Benzaldehyde, anisaldehyde, and cuminaldehyde cannot be estimated by this method. E. W. W.

Euphorbium. ALEXANDER TSCHIRCH and PAUL (*Arch. Pharm.*, 1905, **243**, 249—291).—Some difficulty was experienced in obtaining a sample of the resin fairly free from vegetable and earthy impurities. The specimen examined had acid number 36—39, saponification number 80—110, methyl number 1·68. The following percentages were soluble in the solvents named: alcohol (of 50, 60, 75, 90, 96 per cent. by volume respectively), 34, 44, 50, 62, 74—75; ether, 56; acetone, 80; chloroform, 60; ethyl acetate, 62; toluene, 62; amyl alcohol, 74; carbon disulphide, 88; light petroleum, 36; acetic acid, 96; water, 32·5. The part soluble in ether had acid number 40, and saponification number 100; that soluble in alcohol had acid number 19. The ash amounted to 4·1 per cent. when ignited over the blowpipe, to 8 per cent. when heated over the bunsen burner; it consisted mainly of calcium oxide or carbonate respectively. The crude resin contains a trace of nitrogen, but the purified resin contains none. When a filtered light petroleum extract of the resin is floated on a solution of one drop of concentrated sulphuric acid in 20 c.c. of water, a very stable blood-red layer is formed at the surface where the two liquids touch; on shaking, the whole of the acid liquid becomes red, and this colour only slowly changes to brown. The reaction may be used for purposes of identification; an extract of the most suitable concentration is obtained from 0·1 gram of euphorbium and 10 c.c. of light petroleum.

From an ethereal solution of the resin, 1 per cent. aqueous ammonium carbonate extracts *euphorbic acid*, $C_{24}H_{30}O_6$, which is amorphous, melts at 107—108°, and has acid number 130—135, corresponding with monobasicity, and saponification number 204.

From the residual ethereal solution, no appreciable amount of anything was extracted by 1 per cent. aqueous sodium carbonate or sodium hydroxide.

Concentrated aqueous sodium hydrogen sulphite extracted a very small quantity, about 0·005 per cent., of a substance which melted at 126° and gave several of the reactions of an *aldehyde.*

The ethereal solution remaining was evaporated; the residue was freed from euphorbone by extraction with light petroleum, mixed with aqueous potassium hydroxide, and distilled with steam for weeks. The aqueous distillate contained practically nothing, so that no essential oil can have been present. Undissolved, there remained a small quantity of *euphorboresen*, $C_{33}H_{48}O_4$, which is amorphous and melts at 74—76°. When the residual alkaline liquid was acidified, *a-euphorboresen*, $C_{28}H_{48}O$, was precipitated as an amorphous substance melting at about 75° and now insoluble in dilute aqueous potassium hydroxide; the liquid still contained a small quantity of a substance with the character of a *phenol.*

From an aqueous extract of the drug, calcium malate was isolated; also a dextrorotatory *carbohydrate* that was precipitated by alcohol, and another (pentosan?) which remained dissolved. No appreciable amount of any gum was present. Nor could tartaric, citric, or oxalic acid be detected.

Grains of starch were isolated from the drug; these had the shape of dumb-bells or bones, as often happens with the *Euphorbiaceæ.* An amorphous, pungent principle could be extracted from the drug with water, alcohol, or ether.

Euphorbone, $C_{30}H_{48}O$ (molecular weight found 501—517), is best obtained from the drug by extraction with light petroleum and crystallisation first from alcohol and then repeatedly from acetone. It melts at 115—116° and distils and sublimes unchanged under diminished pressure; from light petroleum, it crystallises with some of the solvent, and then melts at 67—68°. It is optically inactive; it does not contain methoxyl or ethoxyl groups, and its iodine number, 101—112, suggests that addition and substitution occur together. Attempts to prepare an acetyl or a benzoyl derivative were unsuccessful. Alcoholic potassium hydroxide is without action, and fusion with potassium hydroxide leads to no definite result. By heating euphorbone with nitric acid of sp. gr. 1·34, an amorphous, yellow *substance* was obtained with the composition $C_{27}H_{51}O_7(NO_2)_2$.

In 100 parts of the drug were found: euphorbic acid, 0·7; euphorbone, 40, and amorphous resens, 21; malates, 25, and carbohydrate, 2; impurities and loss, 11. C. F. B.

Pentose Reactions of Saponins. LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1905, **243**, 247—248).—By means of the phloroglucinol and orcinol reactions, furfuraldehyde has been detected after the following saponins have been boiled with dilute hydrochloric acid (compare Plzák, Abstr., 1903, i, 643). Saponin from *Gypsophila spec.*, *Camellia theifera*, *Polygala senega* (senegin), *Acacia concinna*, *Entada scandens*, *Dialopsis africana*, *Digitalis purpurea* (digitonin), *Guaiacum off.*; saponic acid from *Quillaia saponaria* (quillaic acid) and *Guaiacum off.*, and sapotoxin from *Quillaia saponaria.* These substances must therefore yield pentoses on hydrolysis, and are to be regarded as pentosides.

No furfuraldehyde could be detected in the case of the saponin from *Verbascum sinuatum* and the three from *Sarsaparilla*. C. F. B.

Chlorophyll. Leon Marchlewski (*Zeit. physiol. Chem.*, 1905, **44**, 422—426).—The optical activity of chlorophyll and its derivatives is believed to be due to the green constituent. Hartley's blue chlorophyll is considered to be unchanged chlorophyll. W. D. H.

Oxidation of the Higher Homologues of Aniline on the Fibre. S. Kirpitschnikoff (*Zeit. Farb. Text. Ind.*, 1905, **4**, 233—234).—The following bases, printed on a fabric, may be oxidised to a moderately permanent dye by means of sodium chlorate and potassium ferrocyanide; the colour of the dye is shown in brackets. Aniline (black); *o*-toluidine (dark violet); *m*-toluidine (blackish-violet); *p*-toluidine (chestnut-brown); xylidine (black); cumidine (brown with a rose shade). W. A. D.

Brown Sulphur Dye from 2:4:5-Triaminotoluene. Kalle & Co. (D.R.-P. 157540).—When fused with sodium sulphide and sulphur at 160°, 2:4:5-triaminotoluene yields a remarkably fast brown dye. In place of triaminotoluene, the more readily accessible benzeneazo-*m*-tolylenediamine may be employed; in this case, the product is afterwards heated at 220° to remove aniline. C. H. D.

Sulphur Dye from 2:2′-Diamino-4:4′-oxalotoluidide. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 157103).—A yellow dye resembling that obtained by fusing 2:2′-diamino-4:4′-oxalotoluidide with sulphur (this vol., i, 249), but having greater fastness towards alkalis, may be prepared by melting the diamino-oxalotoluidide with 2 mols. of *m*-tolylenediamine at 150—200° and fusing the product with sulphur at a temperature above 170°. C. H. D.

Derivatives of Dihydro*iso*benzofuran. Alfred Guyot and J. Catel (*Compt. rend.*, 1905, **140**, 1348—1350. Compare this vol., i, 226).—When phenylphthalide is added to a solution of magnesium phenyl bromide in ether, there is formed *o*-benzhydryltriphenylcarbinol, $OH\cdot CPh_2\cdot C_6H_4\cdot CHPh\cdot OH$, but when the two reagents are mixed in the reverse order there is obtained *2-hydroxy* 1:2-*diphenyl*-1:2-*dihydro*iso*benzofuran*, $C_6H_4<\begin{matrix}CHPh\\CPh(OH)\end{matrix}>O$, which forms small, colourless crystals, dissolves in organic solvents, and readily loses a mol. of water when heated alone or when boiled in acetic acid or in alcohol containing some hydrogen chloride, yielding a *substance* which crystallises in golden-yellow leaflets, melts at 125°, and dissolves in benzene with a green fluorescence. This new substance, on reduction with sodium amalgam, furnishes 1:2-*diphenyl*-1:2-*dihydro*iso*benzofuran* (m. p. 96°), and is oxidised by potassium dichromate in acetic acid to *o*-dibenzoylbenzene, whence the authors conclude that it has the constitution $C_6H_4<\begin{matrix}CPh\\|\\CPh\end{matrix}>O$ or $C_6H_4\ll\begin{matrix}CPh\\CPh\end{matrix}>O$.

o-Dibenzoylbenzene yields a *diphenylhydrazone* melting at 165° and

a *phthalazine*, $C_6H_4<\begin{matrix}CPh:N\\ \mid\\ CPh:N\end{matrix}$, which melts at 192° and is soluble in acids, and furnishes a crystalline *platinichloride*. When either 2-hydroxy-1 : 2-diphenyl-1 : 2-dihydro*iso*benzofuran or *o*-dibenzoylbenzene is reduced with sodium amalgam, *o-dibenzhydrylbenzene*,

$$C_6H_4(CHPh{\cdot}OH)_2,$$

is produced. This melts at 128° and, when heated in acetic acid solution with hydrochloric acid, yields the 1 : 2-diphenyl-1 : 2-dihydro*iso*benzofuran mentioned above. T. A. H.

Basicity of Pyronic Oxygen. Halogen Double Salts of Metals and Dinaphthapyryl. ROBERT FOSSE and L. LESAGE (*Compt. rend.*, 1905, **140**, 1402—1403).—The dinaphthapyryl group,

$$CH\frac{\diagup C_{10}H_6 \diagdown}{\diagdown C_{10}H_6 \diagup}O- \quad \text{or} \quad -CH<\begin{matrix}C_{10}H_6\\ C_{10}H_6\end{matrix}>O,$$

has basic properties, and a number of halogen double salts have been prepared in which this group plays the *rôle* of an atom of an alkali metal. The formulæ of the double chlorides and bromides are given below, the dinaphthapyryl group being represented by R.

$AuCl_3,RCl$, microscopic red crystals.
$HgBr_2,RBr$, red, yellow by reflected light.
$CuBr_2,RBr$, green.
$FeBr_3,RBr$, red, yellow by reflected light.
$PtCl_4,2RCl$,
$PtCl_2,2RCl$, green crystals.
$CdBr_2,2RBr$, red, green in reflected light.
$MnBr_2,2RBr$, red, yellow in reflected light.
$CoBr_2,2RBr$, red, metallic shimmer.

The double salts are represented as containing quadrivalent basic oxygen corresponding with the first formula for the dinaphthapyryl group. H. M. D.

Origin of Alkaloids in Plants. AMÉ PICTET (*Arch. Sci. phys. nat.*, 1905, [iv], **19**, 329—352).—The alkaloids in the plant economy correspond with the urea, uric acid, glycine, &c., in the animal system. They are localised in special tissues and are the nitrogenous products of cell metabolism arising from the breaking down of more complex substances and subsequent chemical modification by condensation with other compounds present in the plant, the most common of these changes being the methylation of possibly noxious hydroxyl or imino-groups by means of formaldehyde according to the equations $R{\cdot}OH + CH_2O = R{\cdot}OMe + O$; $R{:}NH + CH_2O = R{:}NMe + O$; $R(OH)_2 + CH_2O = R<\begin{matrix}O\\ O\end{matrix}>CH_2 + H_2O$ (Eschweiler, this vol., i, 328). The alkaloids containing the pyrrole or indole ring (nicotine, atropine, cocaine, hygrine, strychnine, or brucine) are degradation products of proteids (Fischer, Abstr., 1901, i, 745, 780; Nencki, Abstr., 1901, i, 434, 554), but the pyridine, piperidine, or quinoline ring characteristic of the alkaloids of hemlock, quinine, opium, &c., does not occur in proteids, nucleins, lecithins, or any other complex vegetable product, and the author is of opinion that these rings are formed by an intramolecular transformation of a methylated pyrrole or indole ring; such

transformations can be effected by the action of heat, the author having obtained pyridine from 1-methylpyrrole or 2-methylpyrrole; quinoline from 1-methylindole; *iso*quinoline from methylphthalimidine, and phenanthridine from methylcarbazole (compare Abstr., 1904, i, 771). M. A. W.

Aminocodeine. EDUARD VONGERICHTEN and CARL WEILINGER (*Ber.*, 1905, **38**, 1857—1859).—The *methiodide*, $C_{18}H_{20}O_5N_2$,MeI, is formed by boiling nitrocodeine with methyl iodide in methyl-alcoholic solution; when boiled with 25 per cent. aqueous sodium hydroxide, it forms nitromorphimethine, $C_{19}H_{22}O_5N_2$, which crystallises in yellow needles and melts at 214—215°. The *methiodide*, $C_{19}H_{22}O_5N_2$,MeI, crystallises in yellow needles.

When reduced with tin and glacial acetic acid, nitrocodeine forms *diacetylaminocodeine*, $C_{22}H_{26}O_5N_2$, which crystallises in flat, white needles, melts at 120°, and forms the *methiodide*, $C_{22}H_{26}O_5N_2$,MeI. This crystallises in white needles, melts at 251—252°, and when boiled with silver acetate and acetic anhydride, the reaction mixture being afterwards heated in a sealed tube at 160—170°, forms *triacetylaminomethylmorphol*, $C_{21}H_{21}O_5N$, which crystallises in yellow needles, melts at 178—179°, and dissolves in alcoholic sodium hydroxide to a brown solution. Oxidation of the triacetyl compound leads to the formation of a *quinone* which contains nitrogen; it is obtained as a yellow precipitate on addition of sulphuric acid to its solution in aqueous sodium hydrogen sulphite, and dissolves in alcoholic sodium hydroxide to a green solution which becomes red on addition of acetic acid. On solution of the quinone in aqueous sodium hydroxide and precipitation with acetic acid, the *amino-quinone* is obtained as a dark blue, flocculent substance which dissolves in alcohol or chloroform to red solutions. A *substance* which crystallises in red needles, melts at 240°, and dissolves in concentrated sulphuric acid, or in alcoholic sodium hydroxide to red solutions, is formed as a by-product in the oxidation of the triacetyl compound.

The properties of the quinone show that the nitro-group of nitrocodeine must have replaced a hydrogen atom of the phenanthrene diphenyl nucleus. G. Y.

Derivatives of Morphenol. EDUARD VONGERICHTEN (*Ber.*, 1905, **38**, 1851—1857. Compare Abstr., 1898, i, 98; Abstr., 1901, i, 742). —α-Bromomorphenol methyl ether, obtained as previously described from bromomethylmorphimethine, the *methiodide* of which melts at 252°, yields on oxidation a diphenanthryl derivative,

$$C_{15}H_7O_2Br\cdot O\cdot C_{15}H_7O_2Br,$$

melting at 330°, and a small amount of a bromo-quinone which forms condensation products with *o*-diamines.

β-Bromomorphenol methyl ether is formed by the action of bromine on acetylmorphenol and hydrolysis of the acetylbromomorphenol (m. p. 208°) by means of sodium methoxide in a sealed tube at 100°. Both bromomorphenol methyl ethers melt at 124°, but a mixture of the two melts at 95—98°. Oxidation of the β-bromo-ether with chromic acid in glacial acetic acid solution leads to the formation of reddish-

brown amorphous products and not to a crystalline quinone, whereas by the oxidation of acetylbromomorphenol there is obtained a *bromomorphenolquinone*, which dissolves in aqueous sodium hydroxide to a carmine solution and condenses with *o*-tolylenediamine to a yellow, crystalline *azine*, $C_{23}H_{13}O_3N_2Br$. The action of bromine on the α-bromoether leads to the formation of a *dibromomorphenol methyl ether*, $C_{15}H_8O_2Br_2$, which crystallises in needles and melts at 203°; with bromine in carbon disulphide solution, the β-bromo-ether forms an *additive* compound, which separates in nodular crystals and, when heated at 105—120°, loses hydrogen bromide and forms a *dibromomorphenol methyl ether*, melting at about 200°. G. Y.

1-Methylpyrrolidine from Nicotine. Amé Pictet (*Ber.*, 1905, **38**, 1951—1952).—By the action of silver oxide on nicotine, at least three other substances are formed in addition to nicotyrine, and these may be separated from one another and from unchanged nicotine by distillation in a vacuum.

The first fraction consisted of 1-methylpyrrolidine, which boils at 81—82°, has an odour of piperidine, and is strongly alkaline. It was further identified by means of its aurichloride, hydrochloride, and picrate respectively. A. McK.

Reduction of Metanicotine with Sodium and Absolute Alcohol. Emil Maass (*Ber.*, 1905, **38**, 1831—1832).—*Hexahydrometanicotine*, $CH_2{<}{}^{CH_2\cdot CH_2}_{NH\cdot CH_2}{>}CH\cdot CH\colon CH\cdot CH_2\cdot CH_2\cdot NHMe$, obtained by reducing metanicotine by means of sodium and absolute alcohol, is an optically inactive, clear oil, which boils at 251—252°, has a sp. gr. 0·944 at 15°, is readily soluble in ether, and has an odour closely resembling that of piperidine. T. H. P.

Some Derivatives of ψ-Pelletierine. Richard Willstätter and Hans Veraguth (*Ber.*, 1905, **38**, 1984—1991).—*n*-Methylgranatanine, prepared by Piccinini's method (Abstr., 1898, i, 488), melts at 55—58° and is apparently purer than Ciamician and Silber's base (Abstr., 1894, i, 154), which melted at 49—50°; the *platinichloride* forms short prisms and melts and decomposes at 220—221°.

N-Methylgranataninemethylammonium hydroxide,

$$\begin{array}{lll} CH_2-CH & \text{———} & CH_2 \\ | & | & | \\ CH_2 & NMe_2\cdot OH & CH_2 \\ | & | & | \\ CH_2-CH & \text{———} & CH_2 \end{array},$$

prepared from the corresponding methiodide by means of silver oxide, crystallises in hard, rectangular, efflorescent plates, containing about $16H_2O$. On distilling, the ammonium base loses water giving Δ^4-des-*dimethylgranatanine*, $CH_2{<}{}^{CH_2\cdot CH(NMe_2)\cdot CH_2}_{CH_2\cdot CH\colon CH—CH_2}$, which is a colourless oil with a narcotic odour and boils at 89·5—92° under 14·5 mm. pressure; it has a sp. gr. 0·916 at 0°/4°. The *picrate* forms flat prisms and melts at 155°; the *platinichloride* forms slender needles and melts and decomposes at 178—180°; the *methiodide*

crystallises from alcohol in long needles and melts and decomposes at 264°.

In addition to *N*-methylgranatanine, the electrolytic reduction of ψ-pelletierine gives rise to a mixture of ψ-methylgranatoline (Ciamician and Silber's methylgranatoline) and a new base, stereoisomeric with the latter, which is called *methylgranatoline*, on account of its appearing more closely analogous with tropine than is Ciamician and Silber's compound; it crystallises from light petroleum in prisms, melts at 69—70°, is more hygroscopic and more soluble in light petroleum than ψ-methylgranatoline, and is easily oxidised by potassium permanganate to ψ-pelletierine. It is transformed into ψ-methylgranatoline by boiling with sodium amyloxide solution. Methylgranatoline *aurichloride* forms sheaves of prisms and melts and decomposes at 210—211°. The *hydrochloride*,

$$C_{16}H_{21}O_2N,HCl,$$

of the benzoyl derivative of methylgranatoline crystallises from alcohol in nodular aggregates of needles and melts at about 182°. The *benzoyl* derivative of ψ-methylgranatoline forms reticular aggregates of needles and melts at 34°; its *hydrochloride* forms rhombohedra melting at 235° and its *hydriodide* crystallises in prisms melting at 242—243°.

des-*ψ-Dimethylgranatoline*, $OH\cdot C_8H_{12}\cdot NMe_2$, obtained by the "exhaustive" methylation of ψ-methylgranatoline, boils at 141—142° under 13·5 mm. pressure; it is accompanied by an *isomeride*, $C_{10}H_{19}ON$, which boils at 113—115° under 16·5 mm. and at 234·5—238·5° (corr.) under the ordinary pressure. The nature of the latter is uncertain, but its behaviour on benzoylation shows that it contains a hydroxyl group. 3-*Chloro-ψ-methylgranatanine*, $C_9H_{16}NCl$, obtained by the action of a mixture of phosphorus oxychloride and pentachloride on the alkamine, crystallises from light petroleum in needles, melts at 56°, and boils at 117—118° under 18 mm. pressure. 3-*Chlorotropane*, $C_8H_{14}NCl$, prepared similarly from tropine, boils at 105—105·5° under 21 mm. pressure. W. A. D.

Oxidation of Sparteine. RICHARD WILLSTÄTTER and WILHELM MARX (*Ber.*, 1905, 38, 1772—1780. Compare Ahrens, Abstr., 1893, i, 232; 1894, i, 150; 1897, i, 231; and Willstätter and Fourneau, Abstr., 1902, i, 557).—On oxidising sparteine sulphate with an amount of chromic acid corresponding with 6 atoms of oxygen, an unsaturated base, *spartyrine*, $C_{15}H_{24}N_2$, is obtained, which, although having the same composition as Ahrens' dehydrosparteine, differs completely from it; it crystallises from ethyl acetate, melts at 153—154°, has $[\alpha]_D - 25{\cdot}96°$ at 18·5°, and gives a hygroscopic *hydrochloride*, $C_{15}H_{26}N_2Cl_2,H_2O$; the *platinichloride*, $C_{15}H_{26}N_2Cl_6Pt,3H_2O$, forms orange-yellow needles. As spartyrine contains a double linking, the oxidation of sparteine probably occurs thus:

$$\genfrac{}{}{0pt}{}{C}{C}\!\!>CH\cdot CH< \longrightarrow \genfrac{}{}{0pt}{}{C}{C}\!\!>C(OH)\cdot CH< \longrightarrow \genfrac{}{}{0pt}{}{C}{C}\!\!>C{:}C< .$$

When double the quantity of chromic acid is used in oxidising sparteine, the principal product is oxysparteine, $C_{15}H_{24}ON_2$, which melts at 87·5° instead of 84° as stated by Ahrens; it boils at 209°

under 12·5 mm. pressure, has $[\alpha]_D - 10{\cdot}04°$ at 18°, and resists the action of potassium permanganate and chromic acid. The *platinichloride*, $C_{15}H_{26}ON_2Cl_6Pt,2H_2O$, forms short prisms, becomes anhydrous at 130°, and melts and decomposes at 225—227°; the *mercurichloride* sinters at 150° and decomposes at 195°; the *thiocyanate* sinters at 80° and melts at 87·5°.

Both spartyrine and oxysparteine are accompanied by another *substance*, $C_{15}H_{24}O_4N_2$, which cannot be obtained in a crystalline condition, is very hygroscopic, and melts and decomposes at 158°; when precipitated by adding alcohol to its solution in acetone, it contains $1H_2O$. It can be further oxidised by chromic acid to a *substance*, $C_{12}H_{22}O_4N_2$, which resembles the compound $C_{15}H_{24}O_4N_2$, but separates from acetone on adding alcohol with $\frac{1}{2}$EtOH. W. A. D.

Pyrogenic Transformation of Methylpyrroles into Pyridine Derivatives. Amé Pictet (*Ber.*, 1905, **38**, 1946—1951. Compare Pictet and Steinmann, Abstr., 1904, i, 771).—Pyridine is formed when 2-methylpyrrole is distilled through a tube heated to dull redness. It is probable that the 2-methylpyrrole is an intermediate product in the transformation of 1-methylpyrrole into pyridine. 1-Benzylpyrrole (Ciamician and Silber, Abstr., 1887, 843) may be prepared by the distillation of benzylamine mucate. When passed through a hot tube, it yields 3-phenylpyridine.

A 17 per cent. yield of quinoline is obtained by passing the vapour of 2-methylindole through a hot tube, and a 40 per cent. yield of phenanthridine by treating methylcarbazole in a similar manner.

The base obtained by Graebe and Pictet (Abstr., 1889, 141) by distilling methylphthalimidine with zinc dust is *iso*quinoline. J. J. S.

Synthesis of Hydroxypyrrolidinecarboxylic acids (Hydroxyprolines). Hermann Leuchs (*Ber.*, 1905, **38**, 1937—1943).—Ethyl δ-chloro-α-bromo-γ-valerolactone-α-carboxylate (Traube and Lehmann, Abstr., 1901, i, 502) reacts with a cold methyl-alcoholic solution of ammonia yielding the *monoamide* of *chloromethyltrimethyleneoxidedicarboxylic acid*, $O\!<\!\begin{smallmatrix}C(CONH_2)_2\\CH(CH_2Cl)\end{smallmatrix}\!>\!CH_2$, which crystallises from hot water in small needles, melts at 218—219° (corr.), and is insoluble in chloroform, benzene, or ethyl acetate.

When the chlorobromo-ester is hydrolysed with concentrated hydrobromic acid and then heated at 120—130° under reduced pressure, it yields *δ-chloro-α-bromo-γ-valerolactone*, $CH_2Cl{\cdot}CH\!<\!\begin{smallmatrix}O\text{——}CO\\CH_2{\cdot}CHBr\end{smallmatrix}$, as a viscid oil distilling at 156—164° (corr.) under 11 mm. pressure. The crude lactone, when left in contact with concentrated aqueous ammonia, yields a mixture of two isomeric 4-hydroxypyrrolidinecarboxylic acids which are most readily separated by means of their *copper* salts. The copper salt, $Cu(C_5H_8O_3N)_2,4H_2O$, of the α-compound forms deep blue crystals sparingly soluble in water and loses its water of crystallisation at 105°. The corresponding acid, *α-4-hydroxypyrrolidine-2-carboxylic acid*, $NH\!<\!\begin{smallmatrix}CH_2{\cdot}CH(OH)\\CH(CO_2H)\text{—}\end{smallmatrix}\!>\!CH_2$, crystallises in small, six-sided plates, melts

and decomposes at 261° (corr.) when rapidly heated, and dissolves readily in water and only very sparingly in alcohol. It has a sweet taste, and its aqueous solution has a neutral reaction. The *β-naphthalenesulphone* derivative, $C_{10}H_7 \cdot SO_2 \cdot N < \begin{matrix} CH_2 \cdot CH(OH) \\ CH(CO_2H) \end{matrix} > CH_2$, melts at 186—187° (corr.).

The *copper* salt of the *b*-compound, $(C_5H_8O_3N)_2Cu$, is more readily soluble in water, and on the addition of alcohol crystallises in the form of microscopic six-sided, deep blue plates. The *b*-4-*hydroxyproline* (4-*hydroxypyrrolidine*-2-*carboxylic acid*) melts and decomposes at 250° (corr.) and is somewhat less soluble in water or methyl alcohol than the *a*-compound. It has an insipid taste and its aqueous solution has a feebly acid reaction.

Di-β-naphthalenesulpho-b-4-hydroxypyrrolidine-2-carboxylic acid,

$$C_{10}H_7 \cdot SO_2 \cdot N < \begin{matrix} CH_2 \cdot CH(O \cdot SO_2 \cdot C_{10}H_7) \\ CH(CO_2H) \end{matrix} > CH_2,$$

crystallises from organic solvents in minute needles, melts at 181—182° (corr.), and is practically insoluble in water or ether.

J. J. S.

Purification of Pyridine. LÉONCE BARTHE (*Bull. Soc. chim.*, 1905, [iii], 33, 659—661).—The "pure pyridine" of commerce frequently contains the homologues of this base and ammonia. Agitation of the pyridine with distilled water and a solution of sodium hypobromite converts the pyridine into (1) a colourless, odourless liquid *substance*, which contains no bromine and boils at 117—121°, and (2) a crystalline brominated *compound*. Both these products are being further investigated.

Ammonia may be removed from commercial pyridine by shaking it with water and crystalline magnesium hydrogen phosphate, which combines directly with ammonia or the amines to form salts of the type of magnesium ammonium phosphate. Pyridine purified in this way gives only an indefinite wine colour with litmus solution, and consequently titration with standard acid, using litmus as an indicator, may be applied to the estimation of ammonia in pyridine.

T. A. H.

Abnormal Salts of Betaines and Pyridinecarboxylic Acids. RICHARD TURNAU (*Monatsh.*, 1905, 26, 537—561. Compare Goldschmidt and Hönigschmid, Abstr., 1904, i, 86; ii, 94).—When heated with an excess of methyl iodide, with or without water or alcohol as solvent, in a sealed tube at 100° for 6—7 hours, picolinic acid forms the *methiodide*, $\begin{matrix} CH \cdot CH{:}C \cdot CO \cdot O \cdot NMe{=\!=}CH \cdot CH \\ CH \cdot CH{:}NMeI \quad C(CO_2H){:}CH \cdot CH \end{matrix}$, which is formed also by evaporating the methylbetaine of picolinic acid with hydriodic acid. The methiodide crystallises in long, yellow needles, decomposes at 154—158°, is readily soluble in water, but less so in methyl or ethyl alcohol, and is not acted on by boiling water or hydriodic or hydrochloric acid; the *potassium* salt crystallises in long, hygroscopic needles; the *barium* salt, $(C_{14}H_{14}O_4N_2I)_2Ba,4H_2O$, formed by the action of barium carbonate on the methiodide, or of barium iodide on the methylbetaine of picolinic acid, crystallises in white needles, loses

$2H_2O$ at 105°, and melts at 130—150°. When shaken with freshly precipitated silver chloride in aqueous solution, the methiodide is converted into the *methochloride*, $C_{14}H_{15}O_4N_2Cl,HCl$, which crystallises in needles, sinters at 105°, melts at 120°, is strongly hygroscopic when anhydrous, and when repeatedly evaporated with hydrochloric acid yields the *hydrochloride* of the methylbetaine of picolinic acid,

$$C_7H_7O_2N,HCl\,;$$

this decomposes at 165—170°. The *methobromide*, $C_{14}H_{15}O_4N_2Br,H_2O$, formed by the action of silver bromide on the methiodide, melts at 115°, and when evaporated with hydrobromic acid yields the *hydrobromide* of the methylbetaine of picolinic acid, $C_7H_7O_2N,HBr$, which crystallises in short, thick needles and decomposes at about 179°.

When evaporated with hydriodic acid over the water-bath and finally over sodium hydroxide in a vacuum, picolinic acid forms the *hydriodide*, $HI,C_5NH_4\cdot CO\cdot O\cdot C_5NH_3\cdot CO_2H$, which crystallises in small, stout, yellow needles, melts and decomposes at 190—200°, behaves as a tribasic acid on titration, and when shaken with silver chloride and water yields picolinic acid and its hydrochloride.

The action of methyl iodide on nicotinic acid at 150° leads to the formation of the normal *methiodide* (Meyer, Abstr., 1901, i, 190), which melts at about 220° and, when shaken with silver chloride and water, yields the *methochloride*, $C_7H_8O_2NCl$; this crystallises in needles or prisms and melts and decomposes at 245—250°.

When heated with methyl iodide at 150° for 12 hours, *iso*nicotinic acid forms the *methiodide*,
$$\begin{array}{lllll} CO_2H\cdot C\!-\!CH\!:\!CH & & & CH\cdot CH\!:\!NMeI & \\ \quad\;\, \| \qquad\;\; | & & & \;\| \qquad\qquad\; | & \\ \quad\;\, CH\cdot CH\!:\!NMe\cdot O\cdot CO\cdot C\!-\!CH\!:\!CH & & & & \end{array},$$
which crystallises in long, yellow needles or in prisms and plates, melts and decomposes at 247°, and is identical with the intermediate product obtained by Meyer in the preparation of the methylbetaine of *iso*nicotinic acid (*Monatsh.*, 1903, **24**, 201). The action of methyl iodide on anhydrous 2-methylpyridine-6-carboxylic acid leads to the formation of an *additive compound*, but on the acid containing water of crystallisation to the formation of the *hydriodide*,

$$HI,C_5NH_3Me\cdot CO\cdot O\cdot C_5NH_3Me\cdot CO_2H,$$

which is formed also by the action of hydriodic acid on 2-methylpyridine-6-carboxylic acid; it melts at 230°. With ethyl iodide, picolinic and *iso*nicotinic acids form additive compounds which, when shaken with silver oxide and water, yield the corresponding ethylbetaines. The action of allyl iodide on picolinic acid leads to the formation of the hydriodide, $C_{12}H_{10}O_4N_2,HI$, melting at 190—200°.

G. Y.

Derivatives of Iodoquinolines with Multivalent Iodine. Conrad Willgerodt [and, in part, Paul Frischmuth] (*Ber.*, 1905, **38**, 1805—1811).—8-*Iodo*-6-*methylquinoline*, prepared from 8-amino-6-methylquinoline by means of the diazo-reaction, is volatile in steam, crystallises from alcohol in six-sided prisms, and melts at 66°; the *sulphate*, $C_{10}H_8NI,H_2SO_4$, forms yellow needles and melts at 180°; the *nitrate*, $C_{10}H_8NI,HNO_3$, melts at 151°; the *hydrochloride* melts at 216°, the *platinichloride* melts and decomposes at 226°, and the *dichromate*, $2C_{10}H_8NI,H_2Cr_2O_7$, melts at 112°.

6-*Methylquinolyl*-8-*iodinium chloride*, $C_{10}H_8N\cdot ICl_2$, obtained by passing chlorine through a solution of 8-iodo-6-methylquinoline in glacial acetic acid, melts and decomposes at 138°.

8-*Iodoso*-6-*methylquinoline*, $C_{10}H_8N\cdot IO$, forms a yellowish-white, amorphous powder and melts and explodes at 175°; the *acetate*,

$$C_{10}H_8N\cdot I(OH)\cdot OAc,$$

crystallises from glacial acetic acid in slender, colourless needles, darkens at 165°, and melts and decomposes at 186°; the *nitrate*, $C_{10}H_8N\cdot I(OH)\cdot NO_3$, explodes at 130°, and the *sulphate*,

$$C_{10}H_8N\cdot I(OH)\cdot SO_4H,$$

melts and decomposes at 102°.

8-*Iodoxy*-6-*methylquinoline*, $C_{10}H_8N\cdot IO_2$, separates from water in colourless crystals and explodes violently at 187°.

Di-6-*methylquinolyl*-8-*iodinium hydroxide*, $(C_{10}H_8N)_2I\cdot OH$, prepared by the action of silver oxide and water on a mixture of the iodoxy- and iodoso-compounds, was obtained only in solution; the *chloride*, $(C_{10}H_8N)_2ICl$, forms slender, white needles melting at 186°; the corresponding *bromide* crystallises from dilute alcohol in small needles and melts at 174°, and the *iodide* melts at 162°. The *dichromate*,

$$[(C_{10}H_8N)_2I]_2Cr_2O_7,$$

decomposes at 190°, the *platinichloride*, $C_{40}H_{32}N_4I_2Cl_6Pt$, at 190°, and the *mercurichloride* melts and decomposes at 144°.

p-*Tolyl*-6-*methylquinolyl*-8-*iodinium hydroxide*,

$$C_{10}H_8N\cdot I(C_7H_7)\cdot OH,$$

prepared from *p*-iodoxytoluene and 2-iodoso-4-methylquinoline, gives the following crystalline salts. The *chloride*, $C_{10}H_8N\cdot I(C_7H_7)Cl$, begins to decompose at 174° and melts at 194°; the *bromide* melts at 164°, the *iodide* melts and decomposes at 157°, the *dichromate* decomposes at 160°, and the *platinichloride* at 226°. W. A. D.

Dyes from Quinolinium Compounds. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 158078).—2-Methylquinoline (quinaldine) combines with alkyl sulphates to form highly hygroscopic methylquinolinium alkyl sulphates. Alkali hydroxides convert these into red or violet dyes, which contain 1 atom of sulphur to 2 mols. of quinaldine, and have active sensitising properties when added to silver haloid emulsions.

2-*Methylquinolinium ethosulphate*, $C_9NH_6Me\cdot NEt\cdot SO_4Et$, reacts with alcoholic sodium hydroxide, yielding dark red, metallic crystals, soluble in water, alcohol, chloroform, or acetone, insoluble in ether or benzene. Dilute acids dissolve the compound to colourless solutions. 2-*Methylquinolinum methosulphate* reacts in similar manner. C. H. D.

Action of Formaldehyde and Sodium Hydrogen Sulphite on Aromatic Diamines. MAURICE PRUD'HOMME (*Bull. Soc. Ind. Mul.*, 1905, 43—44).—When benzidine, dissolved in dilute hydrochloric acid, is added to a mixture of formaldehyde with excess of sodium hydrogen sulphite, a crystalline *substance* separates, to which the formula

$$CH_2[N(CH_2\cdot SO_3Na)\cdot C_6H_4\cdot C_6H_4\cdot NH_2]_2$$

is ascribed. This yields a yellowish-green diazo-compound which combines with phenols, amines, or acids yielding dyes, which

are readily soluble and dye cotton and wool directly (the latter best in an acid bath), and are less sensitive to acids than the corresponding benzidine derivatives. This reaction also takes place with *p*-phenylenediamine, the tolidines, and other aromatic diamines. T. A. H.

Composition of Benzidine Chromate. A. KOTSCHUBEY (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 349—351).—The author's analyses of the blue insoluble compound obtained by the action of potassium dichromate on benzidine (compare Julius, Abstr., 1884, 1181) point to its composition being expressed by $C_{12}H_8(NH_2)_2,CrO_3$. T. H. P.

Reaction of Potassium Ferricyanide with Aromatic Polyamines. JACOB N. BARSILOWSKY (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 337—348).—When dilute aqueous or aqueous-alcoholic solutions of benzidine and potassium ferrocyanide are mixed, a blue, insoluble *compound* is formed having the composition

$$(NH_2\cdot C_6H_4\cdot C_6H_4\cdot NH_2)_4FeCy_6,3H_2O.$$

This compound is produced by the action of the oxygen from the water present on the first-formed *product*, which has the formula

$$(C_{12}H_{12}N_2)_4,H_4FeCy_6,3H_2O$$

and is a colourless substance; when treated with acids or alkalis, this latter is decomposed into hydroferrocyanic acid and benzidine. The oxidation of $(C_{12}H_{12}N_2)_4,H_4FeCy_6,3H_2O$ to

$$(C_{12}H_{12}N_2)_4FeCy_6,3H_2O$$

by air and water is not complete but may be made so by the addition of hydrogen peroxide. T. H. P.

Picryl-, *o*-*p*-Dinitrophenyl-, and 5-Chloro-2-nitrophenyl-2 : 4 : 5-trimethylphenylhydrazines and their Derivatives. CONRAD WILLGERODT and FRANZ HERZOG (*J. pr. Chem.*, 1905, [ii], **71**, 385—398).—s-*Picryl-ψ-cumylhydrazine*, $C_6H_2(NO_2)_3\cdot NH\cdot NH\cdot C_6H_2Me_3$, is formed by the action of picryl chloride on 2 : 4 : 5-trimethylphenylhydrazine-ψ-cumylhydrazine in alcoholic solution at 157·5°, is easily soluble in chloroform, benzene, or carbon disulphide, and is oxidised by chromic acid in cold glacial acetic acid solution to *ψ-cumeneazo-2 : 4 : 6-trinitrobenzene*, $C_6H_2Me_3\cdot N_2\cdot C_6H_2(NO_2)_3$, which crystallises in long, brown needles, and melts at 168°. When boiled with glacial acetic acid, picryl-2 : 4 : 5-trimethylphenylhydrazine yields *ψ-cumeneazo-imino-4 : 6-dinitrobenzene oxide*, $C_6H_2(NO_2)_2{<}\overset{N}{\underset{NO}{|}}{>}N\cdot C_6H_2Me_3$, which crystallises in golden needles, melts at 222°, and, when nitrated with concentrated nitric acid in concentrated sulphuric acid solution at 0°, forms *nitro-ψ-cumeneazoiminodinitrobenzene oxide*,

$$C_6H_2(NO_2)_2{:}N_3O\cdot C_6HMe_3\cdot NO_2;$$

this separates as a yellow, crystalline powder and melts and decomposes at 237°. When boiled with potassium iodide in glacial acetic acid solution in a reflux apparatus, ψ-cumeneazoiminodinitrobenzene oxide is reduced to *ψ-cumeneazoiminodinitrobenzene*, $C_6H_2(NO_2)_2\cdot N_3\cdot C_6H_2Me_3$, which is obtained as a yellow powder, melting at 151°, and dissolving in boiling dilute sodium hydroxide to a yellow solution.

·p-*Dinitrophenyl-ψ-cumylhydrazine*, $C_6H_3(NO_2)_2\cdot N_2H_2\cdot C_6H_2Me_3$,

formed by the action of 6-chloro-1 : 3-dinitrobenzene on ψ-cumylhydrazine in concentrated alcoholic solution, crystallises in matted, yellow needles and melts and decomposes at 198°. *ψ-Cumeneazo-2:4-dinitrobenzene* crystallises in brown needles and melts at 177—178°. *ψ-Cumeneazoiminonitrobenzene oxide,* $NO_2 \cdot C_6H_3 <\overset{N-}{\underset{NO}{|}}> N \cdot C_6H_2Me_3$, crystallises in thick, yellow leaflets and melts at 185°. *ψ-Cumeneazoiminonitrobenzene,* $NO_2 \cdot C_6H_3 <\overset{N}{\underset{N}{|}}> N \cdot C_6H_2Me_3$, crystallises in slender needles, melts at 136·5°, is insoluble in dilute alkali hydroxides, and is reduced by iron and acetic acid or by stannous chloride and hydrochloric acid to *ψ-cumeneazoiminoaminobenzene,*

$$NH_2 \cdot C_6H_3 <\overset{N}{\underset{N}{|}}> N \cdot C_6H_2Me_3,$$

which crystallises in brown, transparent leaflets and melts at 147—148°; the *hydrochloride,* $C_{15}H_{16}N_4,HCl$, melts and decomposes at 247·5°; the *sulphate,* $(C_{15}H_{16}N_4)_2,H_2SO_4$, forms white needles; the *platinichloride,* $(C_{15}H_{16}N_4)_2,H_2PtCl_6$, forms an amorphous, yellow powder.

5-*Chloro-2-nitrophenyl-ψ-cumylhydrazine,*

$$NO_2 \cdot C_6H_3Cl \cdot N_2H_2 \cdot C_6H_2Me_3,$$

is formed by the action of 1-chloro-3 : 4-dinitrobenzene on ψ-cumylhydrazine in boiling alcoholic solution. It is obtained as an orange-yellow, crystalline powder, which melts and decomposes at 154°. *ψ-Cumeneazo-5-chloro-2-nitrobenzene,* $C_6H_2Me_3 \cdot N_2 \cdot C_6H_3Cl \cdot NO_2$, crystallises in orange-red needles and melts at 178°. *ψ-Cumeneazoimino-5-chlorobenzene oxide,* $C_6H_3Cl <\overset{N-}{\underset{NO}{|}}> N \cdot C_6H_2Me_3$, crystallises in yellow needles and melts at 137°. *ψ-Cumeneazoiminochlorobenzene,* $C_{15}H_{14}N_3Cl$, crystallises in slightly yellow needles and melts at 115°.

s-*Acetyl-ψ-cumylhydrazide,* $C_6H_2Me_3 \cdot NH \cdot NHAc$, formed by boiling ψ-cumylhydrazine with glacial acetic acid, crystallises in white leaflets and melts at 147°. s-*Benzoyl-ψ-cumylhydrazide* is colourless and melts at 164°. G. Y.

p-Xylylhydrazine, and Picryl-, o-p-Dinitrophenyl-, and 5-Chloro-2-nitrophenyl-p-xylylhydrazines. CONRAD WILLGERODT and WILLY LINDENBERG (*J. pr. Chem.*, 1905, [ii], 71, 398—409).—p-*Xylylhydrazine,* $C_6H_3Me_2 \cdot NH \cdot NH_2$, is formed by reduction of sodium p-xylenediazonium sulphite with zinc dust and acetic acid, decomposition of the product with hydrochloric acid, and liberation of the hydrazine by treatment with sodium hydroxide; it crystallises in glistening, white, slender needles, melts at 78°, and decomposes when exposed to air and light. The *hydrochloride,* $C_8H_{12}N_2,HCl$, crystallises in glistening, slender needles and melts at 212°; the *platinichloride,* $(C_8H_{12}N_2)_2,H_2PtCl_6$, forms a yellow powder; the *sulphate,* $C_8H_{12}N_2,H_2SO_4$, forms colourless crystals; the *nitrate,* $C_8H_{12}N_2,HNO_3$, crystallises in glistening scales. p-*Xylylbenzylidenehydrazine* forms yellow crystals and melts at 110°; *benzophenone*-p-*xylylhydrazone* forms a yellow, crystalline powder and melts at 103°.

s-*Picryl*-p-*xylylhydrazine,* $C_6H_2(NO_2)_3 \cdot N_2H_2 \cdot C_6H_3Me_2$, formed by the

action of picryl chloride on *p*-xylylhydrazine in alcoholic solution, crystallises in small, red, slender needles, melts and decomposes at 169°, is stable when dry, and when boiled with glacial acetic acid in a reflux apparatus yields p-*xyleneazoimino*-4 : 6-*dinitrobenzene oxide*, $C_6H_2(NO_2)_2{<}\overset{N}{\underset{NO}{|}}{>}N{\cdot}C_6H_3Me_2$, which crystallises in golden needles, melts at 235°, and is soluble in most organic solvents. p-*Xyleneazoiminodinitrobenzene*, $C_6H_2(NO_2)_2{<}\overset{N}{\underset{N}{|}}{>}N{\cdot}C_6H_3Me_2$, is formed when picryl-*p*-xylylhydrazine is heated with alcohol in a sealed tube at 120° for 2—3 hours, or when *p*-xyleneazoiminodinitrobenzene oxide is boiled with 1 mol. of potassium iodide and a little water in glacial acetic acid solution in a reflux apparatus; it crystallises in yellow needles and melts at 125°. When boiled with 4 mols. of potassium iodide in glacial acetic acid for 2 days, *p*-xyleneazoiminodinitrobenzene oxide is reduced to a *substance*, $C_{14}H_{11}O_3N_5$, which crystallises in yellow needles and melts at 128°.

p-*Xyleneazotrinitrobenzene*, formed by oxidation of picryl-*p*-xylylhydrazine with chromic acid in glacial acetic acid solution, crystallises in brown needles and melts at 172°.

o-p-*Dinitrophenyl*-p-*xylylhydrazine*, $C_6H_3(NO_2)_2{\cdot}N_2H_2{\cdot}C_6H_3Me_2$, formed from *p*-xylylhydrazine and 1-chloro-2 : 4-dinitrobenzene, crystallises in small, slender needles and melts at 190°. p-*Xyleneazoimino*-p-*nitrobenzene oxide* forms yellow crystals and melts at 167°. p-*Xyleneazoimino*-p-*nitrobenzene* crystallises in yellow needles and melts at 158°. p-*Xyleneazoimino*-p-*aminobenzene*, $NH_2{\cdot}C_6H_3{<}\overset{N}{\underset{N}{|}}{>}N{\cdot}C_6H_3Me_2$, forms a green, crystalline powder, melts at 195°, and forms fluorescent solutions; the *platinichloride*, $(C_{14}H_{14}N_4)_2,H_2PtCl_6$, forms a yellowish-red powder.

p-*Xyleneazoiminobenzene* is a white, flocculent substance, which melts at 136° and is volatile in a current of steam.

p-*Xyleneazo*-2 : 4-*dinitrobenzene* crystallises in glistening, red needles and melts at 157°.

5-*Chloro*-2-*nitrophenyl*-p-*xylylhydrazine*, $C_6H_3Me_2{\cdot}N_2H_2{\cdot}C_6H_3Cl{\cdot}NO_2$, formed from *p*-xylylhydrazine and 1-chloro-3 : 4-dinitrobenzene, crystallises in slender, red needles and melts at 144°. p-*Xyleneazoimino*-5-*chlorobenzene oxide*, $C_6H_3Cl{<}\overset{N}{\underset{NO}{|}}{>}N{\cdot}C_6H_3Me_2$, crystallises in yellow leaflets, melts at 119°, and on reduction with potassium iodide and glacial acetic acid yields a dark oil. p-*Xyleneazo*-5-*chloro*-2-*nitrobenzene*, $C_6H_3Me_2{\cdot}N_2{\cdot}C_6H_3Cl{\cdot}NO_2$, forms small, red crystals and melts at 132°.

s-*Acetyl*-p-*xylylhydrazide*, $C_6H_3Me_2{\cdot}NH{\cdot}NHAc$, forms white crystals and melts at 196°. s-*Benzoyl*-p-*xylylhydrazide* forms glistening, white crystals and melts at 181°. G. Y.

_p_-Ethylphenylhydrazine, Picryl- and _o_-_p_-Dinitrophenyl-_p_-ethylphenylhydrazines and their Derivatives. Conrad Willgerodt and Hans Harter (*J. pr. Chem.*, 1905, [ii], 71, 409—416).—p-*Ethylphenylhydrazine*, $C_6H_4Et{\cdot}N_2H_3$, is formed on reduction of sodium

p-ethylphenyldiazonium sulphite, treatment of the product with hydrochloric acid, and liberation of the hydrazine by means of dilute ammonia; it crystallises in glistening leaflets and is unstable even in the form of its salts. The *hydrochloride*, $C_8H_{12}N_2,HCl$, crystallises in white leaflets and melts at 200°; the *platinichloride*, $(C_8H_{12}N_2)_2,H_2PtCl_6$, forms a red powder; the *sulphate*, $C_8H_{12}N_2,H_2SO_4$, crystallises in red leaflets and melts at 180°; the *picrate*, $C_8H_{12}N_2,C_6H_3O_7N_3$, crystallises in yellow needles and melts at 122°. p-*Ethylphenylbenzylidenehydrazine*, $C_6H_4Et\cdot NH\cdot N:CHPh$, is obtained as a white, flocculent precipitate which melts at 78°. p-*Ethylphenyltolylidenehydrazine*, $C_{16}H_{18}N_2$, crystallises in yellow needles and melts at 175°.

Picryl-p-*ethylphenylhydrazine*, $C_6H_4Et\cdot NH\cdot NH\cdot C_6H_2(NO_2)_3$, crystallises in slender, red needles and melts at 145°. p-*Ethylbenzeneazoimino*-4 : 6-*dinitrobenzene oxide*, $C_6H_2(NO_2)_2<\genfrac{}{}{0pt}{}{N-}{NO}>N\cdot C_6H_4Et$, crystallises in golden leaflets and decomposes at 200°. p-*Ethylbenzeneazoimino*-4 : 6-*dinitrobenzene*, $C_6H_2(NO_2)_2<\genfrac{}{}{0pt}{}{N}{N}>N\cdot C_6H_4Et$, crystallises in yellow leaflets and melts at 140°. 2 : 4 : 6-*Trinitrobenzeneazo*-p-*ethylbenzene* $C_6H_2(NO_2)_3\cdot N_2\cdot C_6H_4Et$, crystallises in golden leaflets and melts at 192°.

o-p-*Dinitrophenyl*-p-*ethylphenylhydrazine*, $C_6H_3(NO_2)_2\cdot N_2H_2\cdot C_6H_4Et$, is obtained as an oil by mixing alcoholic solutions of *p*-ethylphenylhydrazine and 1-chloro-2 : 4-dinitrobenzene.

p-*Ethylbenzeneazoimino*-p-*nitrobenzene*, $NO_2\cdot C_6H_3<\genfrac{}{}{0pt}{}{N}{N}>N\cdot C_6H_4Et$, formed by boiling 2 mols. of *p*-ethylphenylhydrazine with 1 mol. of 1-chloro-2 : 4-dinitrobenzene in alcoholic solution, crystallises in red leaflets and melts at 125°. p-*Ethylbenzeneazoimino*-p-*aminobenzene*, $NH_2\cdot C_6H_3<\genfrac{}{}{0pt}{}{N}{N}>N\cdot C_6H_4Et$, crystallises in slender, red or yellow needles, melts at 155°, and forms fluorescent solutions; the *platinichloride*, $(C_{14}H_{14}N_3)_2H_2PtCl_6$, forms a yellow powder. G. Y.

Yellow Sulphur Dye from Nitro-α-methylbenziminazole. CHEMISCHE FABRIKEN VORM. WEILER-TER MEER (D.R.-P. 157862).—Nitro-α-methylbenziminazole, $NO_2\cdot C_6H_3<\genfrac{}{}{0pt}{}{N}{NH}>CMe$, best prepared by boiling nitro-*o*-phenylenediamine with glacial acetic acid (compare Heim, Abstr., 1888, 1097), does not yield a dye when heated alone with sulphur, but a mixture of the nitro- or amino-compound with benzidine, when fused with sulphur and sodium sulphide, yields a yellow dye of slightly greenish shade. C. H. D.

Naphthaphenazines. AKT.-GES. FÜR ANILIN-FABRIKATION (D.R.-P. 157861).—*o*-Aminoazo-compounds react with β-naphthol when fused together at 205—215°, forming naphthaphenazines. Thus β-naphthol and chrysoidine yield Nietzki's 8-aminonaphthaphenazine (Abstr., 1888, 843), thus: $C_{10}H_7\cdot OH + NPh:N\cdot C_6H_3(NH_2)_2 = NH_2Ph +$

$H_2O + C_{10}H_6\!<\!\overset{N}{\underset{N}{|}}\!>\!C_6H_4\cdot NH_2$. In similar manner, *o*-aminoazotoluene yields naphthatoluazine. C. H. D.

New Naphthazine Syntheses from *o*-Aminoazo-compounds. FRITZ ULLMANN and J. S. ANKERSMIT (*Ber.*, 1905, 38, 1811—1822).—Naphthazines may be obtained with a good yield by fusing *o*-aminoazo-compounds with substituted naphthols; thus in the case of chrysoidine and β-naphthol, 8-amino-$\alpha\beta$-naphthaphenazine is obtained according to the equation $C_{10}H_7\cdot OH + NPh\!:\!N\cdot C_6H_3(NH_2)_2 =$

$$C_{10}H_6\!<\!\overset{N}{\underset{N}{|}}\!>\!C_6H_3\cdot NH_2 + NH_2Ph + H_2O.$$

8-*Aminonaphthaphenazine hydrochloride* crystallises from dilute acetic acid in red leaflets with a bronze lustre and melts and decomposes at 264°; the *nitrate* forms similarly coloured needles and melts and decomposes at 243°. The *methochloride*, $C_{17}H_{14}N_3Cl$, forms small, red needles with a green reflex and melts at 264°. 8-*Acetaminonaphthaphenazine* crystallises from aniline in yellow needles and melts at 298°.

8-*Amino-9-methyl-αβ-naphthaphenazine*, $C_{10}H_8\!<\!\overset{N}{\underset{N}{|}}\!>\!C_6H_2Me\cdot NH_2$, prepared from β-naphthol and 5-benzeneazotolylene-2 : 4-diamine, crystallises from xylene in bright yellow, concentric aggregates of needles and melts at 249°; the *sulphate* forms small, red, felted needles, the *hydrochloride* melts and decomposes at 283°, and the *acetyl* derivative, $C_{19}H_{14}ON_3$, crystallises from nitrobenzene in yellow needles and melts at 295°.

9-Tolunaphthazine [9-methyl-$\alpha\beta$-naphthaphenazine],

$$C_{16}H_6\!<\!\overset{N}{\underset{N}{|}}\!>\!C_6H_3Me,$$

prepared from *o*-aminoazotoluene and β-naphthol, is identical with Witt's product (Abstr., 1887, 591). Benzeneazo-β-naphthylamine and β-naphthol combine together on fusion to form *s*-$\alpha\beta$-naphthazine (Matthes, Abstr., 1890, 992).

8-*Amino-2-hydroxynaphthaphenazine*, $OH\cdot C_{10}H_5\!<\!\overset{N}{\underset{N}{|}}\!>\!C_6H_4\cdot NH_2$, prepared from chrysoidine and 2 : 7-dihydroxynaphthalene, crystallises from aniline or nitrobenzene in small, yellowish-brown needles and melts at 350°.

8-*Amino-2-hydroxy-9-methyl-αβ-naphthaphenazine*,

$$OH\cdot C_{10}H_5\!<\!\overset{N}{\underset{N}{|}}\!>\!C_6H_2Me\cdot NH_2,$$

prepared from 5-benzeneazotolylene-2 : 4-diamine and 2 : 7-dihydroxynaphthalene, crystallises from aniline in yellowish-brown needles and does not melt at 360°; the *hydrochloride* forms red needles with a bronze-like lustre.

2-*Hydroxy*-s-*αβ-naphthazine*, $C_{10}H_6\!<\!\overset{N}{\underset{N}{|}}\!>\!C_{10}H_5\cdot OH$, prepared from benzeneazo-β-naphthylamine and 2 : 7-dihydroxynaphthalene, crystallises from aniline in greenish-yellow needles and melts at 301°.

On heating benzeneazo-*m*-tolylenediamine with 2 : 3-dihydroxynaphthalene at 150—160°, a mixture of 8-*amino*-6-*hydroxy*-9-*methyl*-$\alpha\beta$-*naphthaphenazine*, $C_{17}H_{13}ON_3$, and 8-*amino*-6-*anilino*-9-*methyl*-$\alpha\beta$-*naphthaphenazine*, $NHPh{\cdot}C_{10}H_5{<}\overset{N}{\underset{N}{|}}{>}C_6H_2Me{\cdot}NH_2$, is obtained. The former crystallises from aniline in yellowish-brown needles, melts at 254°, and gives a *sodium* salt which crystallises in yellow needles ; the latter crystallises from aniline in lustrous, reddish-brown needles and melts at 270·5°.

8-*Amino*-6-*hydroxynaphthaphenazine*, $C_{16}H_{11}ON_3$, prepared from chrysoidine and 2 : 3-dihydroxynaphthalene, forms reddish-brown needles and melts at 263°. W. A. D.

Trihydroxyphenylrosinduline. Kalle & Co. (D.R.-P. 158077 and 158100).—A trihydroxyphenylrosinduline is obtained when *p*-aminophenol is fused at 160—170° with benzeneazo-α-naphthylamine, 1 : 4-naphthylenediamine, or α-naphthylamine. In the last two cases, the presence of an oxidising agent, such as *p*-nitrophenol or α-nitronaphthalene, is necessary. The product is insoluble in water, benzene, or dilute acids, but dissolves in alcohol or dilute alkali hydroxides to bluish-violet solutions. If *m*-nitroaniline or *p*-nitroaniline is employed as the oxidising agent, an equivalent quantity of *p*-aminophenol is saved, and the yield of rosinduline is improved. C. H. D.

Electrolytic Reduction of the Nitrocinnamic Acids. Charles Marie (*Compt. rend.*, 1905, **140**, 1248—1250).—When *m*- and *p*-nitrocinnamic acids are reduced in alkaline solution at a platinum cathode with a current density of 5 amperes per sq. dm., the corresponding azoxy-acids are obtained in 80 per cent. yield ; hydrogen is not evolved until the reaction is practically complete. The azoxycinnamic acids are yellow and insoluble in water and in most of the ordinary solvents, but dissolve to some extent in boiling acetic acid and boiling pyridine. The *m*-acid melts at 335—337° ; the *p*-acid decomposes at 360° without melting. Both acids dissolve in warm concentrated sulphuric acid to intense orange-red solutions. The solution of the *m*-acid when heated at 150—160° turns brown, and on dilution and neutralisation a *substance* separates in yellow plates, which melts at 162° and dissolves in water, alcohol, or benzene. The *sodium* salts of the azoxycinnamic acids are only slightly soluble in water. The *silver* salts are faintly coloured, and the *methyl* and *ethyl* esters crystallise from amyl alcohol in brilliant orange needles.

m-Aminocinnamic acid is a secondary product in the reduction of *m*-nitrocinnamic acid, but practically no *m*-aminohydrocinnamic acid is formed. On the other hand, *p*-aminohydrocinnamic acid is the only secondary product in the reduction of *p*-nitrocinnamic acid. When the quantity of electricity passed through the solution is smaller than that theoretically required for the production of the azoxy-acid, small quantities of *p*-nitrohydrocinnamic acid melting at 161° are obtained. Electrolytic reduction of *p*-aminocinnamic acid at a mercury cathode affords the most convenient method of obtaining the corresponding hydro-acid.

o-Nitrocinnamic acid does not yield an azoxy-acid on electrolytic reduction. H. M. D.

Conversion of Diazoamino-*p*- into Aminoazo-*p*-toluene in the Solid State. Coenraad L. Jungius (*Chem. Centr.*, 1905, i, 1464—1465; from *Chem. Weekblad*, 2, 246—249).—The velocity with which the change of diazoamino-*p*-toluene into aminoazo-*p*-toluene takes place at the ordinary temperature has been followed during a period of $1\frac{1}{4}$ years. Mixtures were made by melting together 25 grams of *p*-toluidine (m. p. 45°) with 2·812 grams of diazoamino-*p*-toluene and quantities of *p*-toluidine hydrochloride varying from about 0·7—2·9 grams and quickly cooling the mass. The quantity of nitrogen which was evolved when the mass was treated with dilute sulphuric acid was determined from time to time. Pure diazoamino-*p*-toluene (m. p. 116°) was found to change more slowly than less pure preparations. The extremely small initial velocity increases rapidly, the *p*-toluidine hydrochloride possibly acting as a catalytic agent. The change is distinctly apparent, however, when the hydrochloride is not present, but as the quantity of this salt is increased, the velocity also increases, although not proportionately. Aminoazo-*p*-toluene can also be detected when the substances are merely mixed together and not melted. The maximum change was observed in the case of a mixture obtained by melting together 25 grams of toluidine with 2·812 grams of diazoamino-*p*-toluene and 2·870 grams of toluidine hydrochloride, 94 per cent. being converted into the aminoazo-compound in 13 months. E. W. W.

Carbohydrates from Serum Globulins. III. Leo Langstein (*Monatsh.*, 1905, 26, 531—535. Compare Abstr., 1903, i, 734; 1904, i, 790).—Serum globulin, which had been washed with hot water for 4 weeks, dried, and extracted with alcohol, yielded dextrose when treated with 3 per cent. hydrochloric acid. This dextrose is probably in glucoside combination with the albumin. Lævulose is now found not to be present in serum globulin. The total carbohydrates obtained from serum globulin amount to about 1 per cent., of which about 1/3 is dextrose.

Contrary to Abderhalden, Bergell, and Dörpinghaus' statement (Abstr., 1904, i, 640), serum globulin contains glucosamine, which is separated as the hydrochloride from the benzoic esters obtained as previously described. A small amount of a hydroxyamino-acid was obtained by the trypsin digestion of the syrup formed by the action of an aqueous alkali hydroxide on serum globulin, and precipitation with alcohol. G. Y.

Precipitation Limits with Ammonium Sulphate of some Vegetable Proteids. Thomas B. Osborne and Isaac F. Harris (*Amer. J. Physiol.*, 1905, 13, 436—447. Compare Abstr., 1903, i, 871).—Hofmeister's method of fractional precipitation with ammonium sulphate is regarded as a valuable and ready means of separating proteids in solution. The precipitation limits are not characteristic for each proteid, but depend on the conditions existing in the solution at the time of precipitation. In several experiments, the two products ob-

tained, the one by precipitating a large part of the dissolved proteid at a definite degree of saturation, and the other obtained from its filtrate at one-tenth higher saturation, after separation from solution by dialysis were found to have the same limits of precipitation as one another, which limits were lower and wider apart than those between which the separation was first made. The products were also alike in composition and properties.

Vegetable globulins and albumins cannot be separated by means of their precipitation limits with ammonium sulphate; some globulins require more than half saturation and some albumins (such as leucosin) less for precipitation. W. D. H.

Hæmatogen. Hugounenq and Morel (*Compt. rend.*, 1905, **140**, 1065—1067).—The analyses of hæmatogen given by Miescher and Bunge are not concordant. The percentage composition found in the present research was: C, 43·5; H, 6·9; N, 12·6; P, 8·7; Fe, 0·455; Ca, 0·352; Mg, 0·126; S, traces; O, 27·367. The numbers differ a little from those of Bunge, and are attributed to the material having been freed from all traces of fat and albumin. W. D. H.

Fractional Hydrolysis of Optically Active Esters by Lipase. II. Henry D. Dakin (*J. Physiol.*, 1905, **32**, 199—206. Compare Abstr., 1904, i, 1071).—The partial hydrolysis of the inactive esters of mandelic acid and its alkyl derivatives results in the production of a dextrorotatory free acid and a lævorotatory residue of unchanged ester. In those derivatives in which hydroxyl is replaced by a halogen atom, a lævorotatory free acid and a dextrorotatory residue of ester are the resulting products. When a series of allied, optically inactive esters is hydrolysed by lipase, the active components which are most readily attacked have a similar molecular configuration, but not necessarily the same sign of rotation. The partial hydrolysis of an optically inactive ester in which the asymmetric carbon atom is situated in the alkyl instead of the acyl group, as in the other esters examined, also yields optically active products, showing that the enzyme presumably combines with the molecule as a whole.

W. D. H.

Preparation of Pepsin. P. Schrumpf (*Beitr. chem. Physiol. Path.*, 1905, **6**, 396—397).—The mucous membrane from pig's stomach was subjected to pressure, as in Buchner's work on yeast, and the liquid filtered through a Chamberland filter. Pepsin was separated from the filtrate by the cholesterol method. The pepsin solution was proteid-free. In some cases the solution had rennetic properties, in other cases not, a fact which tells against the view of Pawloff and Nencki that pepsin and rennin action are both due to the same molecule. W. D. H.

Organic Chemistry.

Some Reactions of Acetylene. JULIUS A. NIEUWLAND (*Chem. Centr.*, 1905, i, 1585—1586; from *J. Gasbel.*, **48**, 387—388).—When acetylene is reduced electrolytically, using a cathode of calcium carbide, only a minute quantity of ethylene is liberated; the formation of alcohol observed by Billitzer has not been confirmed. In the presence of sulphuric acid, however, acetaldehyde is formed. The platinum possibly acts in the latter case as a catalytic agent, for the aldehyde is also obtained when acetylene is passed through water containing platinum sponge and a small quantity of nitric acid.

Experiments have shown that the explosions which occur when acetylene is treated with chlorine cannot be ascribed solely to the presence of oxygen (compare Mouneyrat, Abstr., 1898, i, 613). Chlorine hydrate does not cause explosions when brought in contact with acetylene or calcium carbide in open vessels, but in closed vessels explosions occur, carbon and hexachloroethane being formed. When chlorine is passed into a solution of acetylene in acetone or acetylene into a solution of chlorine in carbon tetrachloride at 0°, slight explosions take place where the gases mix above the liquid. If the solution of one gas is gradually added below the surface of the solution of the other, the heat of the reaction causes the gases to escape and a cloud of soot containing hexachloroethane is formed, whilst chloroacetone remains in solution. Tetrachloroacetylene is formed by the direct action of the gases at 1—2°; when an appreciable excess of chlorine is used, the gas burns with a small flame at the end of the delivery tube, and hexachloroethane and carbon are formed. Explosions are invariably accompanied by the formation of hexachloroethane: $2C_2H_2 + 5Cl_2 = C_2Cl_6 + 4HCl + 2C$. The energy liberated by this decomposition is sufficient to cause explosion of the rest of the mixture, the reaction $C_2H_2 + Cl_2 = 2HCl + 2C$ taking place. This hypothesis is supported by the fact that when a very rapid stream of acetylene is passed into bromine water cooled by ice, the gas takes fire, although bromine is much less active than chlorine; ethylene also explodes with chlorine under certain conditions.

When chlorine and acetylene are passed into a flask containing boiling water, tetrachloroacetylene is formed without explosion, and at 140° the gases also react quietly, forming tetrachloroacetylene and hexachloroethane; at 270°, the gases, when diluted with hydrogen chloride, also form the same products without explosion. The action of chlorine compounds on acetylene has also been investigated. The experiments have an important bearing on the explosions which sometimes occur in the process of purifying acetylene by means of bleaching powder. E. W. W.

A Simple Method for the Formation and Preparation of Alkyl Haloids. RUDOLF F. WEINLAND and KARL SCHMID (*Ber.*, 1905, **38**, 2327).—Methyl sulphate (or ethyl sulphate) readily reacts in

aqueous solution with potassium iodide, thus: $Me_2SO_4 + KI = MeI + KMeSO_4$. Methyl chloride may be prepared by heating a mixture of potassium methyl sulphate with potassium chloride; when potassium bromide is used in place of potassium chloride, methyl bromide is formed together with other products, whilst, when potassium iodide is used, iodine is evolved. A. McK.

Constitution of Hexyl Iodide from Mannitol. P. Rasetti (*Bull. Soc. chim.*, 1905, [iii], 33, 691—693).—When the hexyl iodide obtained by Hecht's method (this Journal, 1873, 370) from mannitol is treated with potassium cyanide dissolved in alcohol, the mixture of nitriles formed is a colourless, mobile liquid, which boils at 166—168° under atmospheric or at 72° under 27 mm. pressure. The mixture of hexylformamides, obtained by treating the mixed nitriles with sodium hydroxide in alcohol, forms silky needles, and by fractional crystallisation from warm carbon disulphide is separated into α-ethylvaleramide and α-methylhexoamide (compare this vol., i, 561, 562). The hexyl iodide obtained from mannitol is therefore a mixture of the β- and γ-iodohexanes (compare Wanklyn and Erlenmeyer, this Journal, 1863, 223, and Combes and Le Bel, Abstr., 1893, i, 246).

T. A. H.

***aci*-Dinitro-alcohols. I.** Paul Duden and G. Ponndorf (*Ber.*, 1905, 38, 2031—2036).—Aldol formation takes place when aliphatic aldehydes interact with the alkali salts of *aci*-dinitromethane, thus: $R\cdot CHO + NO_2\cdot CH{:}NO_2K = R\cdot CH(OH)\cdot C(NO_2){:}NO_2K$.

Potassium aci-*dinitroethyl alcohol*, $OH\cdot CH_2\cdot C(NO_2){:}NO_2K$, prepared by the action of formaldehyde on potassium *aci*-dinitromethane, crystallises in rhombic plates. Formaldehyde is evolved when its aqueous solution is boiled. The free *acid* is an oil easily soluble in water; when its aqueous solution is boiled, a vigorous evolution of nitric oxide and carbon dioxide occurs, and a *compound*, $C_5H_2O_7N_4$, is formed which crystallises in glistening leaflets and melts and decomposes at 190°.

Potassium aci-*dinitro*iso*propyl alcohol*, $OH\cdot CHMe\cdot C(NO_2){:}NO_2K$, prepared by the action of an excess of acetaldehyde on potassium *aci*-dinitromethane, forms lemon-yellow crystals. The free *acid* is an oil having the sp. gr. 1·33 at 15°/4° and n_D 1·449 at 15°; its aqueous solution decomposes when boiled.

sec.-aci-*Dinitrobutyl alcohol*, $C_4H_8O_5N_2$, is an oil which is sparingly soluble in water; its *potassium* salt forms yellow, glistening leaflets and explodes at 205°.

sec.-aci-*Dinitroamyl alcohol* (aci-*dinitromethylpropylcarbinol*),

$$C_5H_{10}O_5N_2,$$

is a colourless oil; its *potassium* salt forms glistening, yellow leaflets. The dissociation of the latter was examined quantitatively.

A. McK.

Derivatives of ααα-Trichloro*iso*propyl Alcohol. Louis Henry (*Bull. Acad. roy. Belg.*, 1905, 101—121. Compare Abstr., 1904, i, 279, 794, and this vol., i, 110).—When ααα-trichloro*iso*propyl alcohol

dissolved in light petroleum is treated with phosphorus trichloride there are formed (1) trichloropropylene, $CCl_3\cdot CH\colon CH_2$ (this vol., i, 110); (2) *trichloro*iso*propyl dichlorophosphite*, $PCl_2\cdot O\cdot CHMe\cdot CCl_3$; (3) *trichloro*iso*propyl chlorophosphite*, $PCl[O\cdot CHMe\cdot CCl_3]_2$ (a thick liquid, which boils at 210° under 25 mm. pressure, and in contact with water regenerates trichloro*iso*propyl alcohol), and (4) *trichloro*iso*propylphosphite*, $P[O\cdot CHMe\cdot CCl_3]_3$. The formation of the three esters in this reaction indicates that Jaroschenko's rule that the corresponding olefinic hydrocarbon is the principal product of the action of phosphorus trichloride on *sec.*-alcohols (*Chem. Centr.*, 1897, ii, 334) is not generally applicable. Trichloro*iso*propyl dichlorophosphite is a colourless, rather thick liquid, which boils at 223—224° under 758 mm. pressure and at 140° under 70 mm. pressure, has a sp. gr. 1·5870 at 20°, and reacts with chlorine to form *aaa-trichloro*iso*propyl chloride*, $CCl_3\cdot CHMeCl$. This is a colourless, limpid liquid, which boils at 152—153°, has a sp. gr. 1·473 at 20° and n_D 1·4867. The corresponding *bromide*, similarly prepared, boils at 171—172° under 766 mm. pressure and has a sp. gr. 1·775 at 20°.

When *aaa*-trichloro*iso*propyl alcohol is treated with phosphorus pentachloride, trichloropropylene is formed in small amount, and the principal product is a *trichloro*iso*propyl chlorophosphate* having the constitution $POCl[O\cdot CHMe\cdot CCl_3]_2$. This is a viscous liquid, which dissolves in ether and from such solutions separates as a crystalline *additive product*, which reverts to the original substance when dried by exposure over sulphuric acid. It is decomposed by water, forming a *phosphate* of the constitution $HO\cdot PO[O\cdot CHMe\cdot CCl_3]_2$, which is at first viscous and eventually becomes a crystalline magma.

s-*Hexachloro*iso*propyl formal*, $CH_2[O\cdot CHMe\cdot CCl_3]_2$, obtained by the interaction of *aaa*-trichloro*iso*propyl alcohol with trioxymethylene in presence of zinc chloride (compare Stappers, this vol., i, 261), is a colourless, viscous liquid, possessing a strong odour and bitter taste. It boils at 290° under 750 mm. pressure, does not solidify at −80°, has a sp. gr. 1·481 at 20°, and is insoluble in water. T. A. H.

Presence of Acetylmethylcarbinol in certain Commercial Vinegars. Pastureau (*J. Pharm. Chim.*, 1905, [vi], 21, 593—595).—A sample of vinegar, which gave an abundant precipitate when treated with alcohol and reduced Fehling's solution in the cold, was found to contain about 0·3 per cent. of acetylmethylcarbinol. The latter was identified by the melting point (243°) of its osazone and estimated by its silver reducing power. Its presence in the vinegar was probably due to the action of bacteria of the *tartricus* species on the carbohydrates. W. P. S.

Action of Dilute Sulphuric Acid on the Glycol obtained by Reduction of Propionaldol. Julius Munk (*Monatsh.*, 1905, **26**, 663—674. Compare Thalberg, Abstr., 1898, i, 550).—The glycol, $C_6H_{14}O_2$, boils at 100—102° under 14 mm. or at 214° under ordinary pressure, and, when heated with 20 per cent. sulphuric acid at 100° in a sealed tube, yields principally the dioxide, $C_{12}H_{24}O_2$, along with small quantities of an unsaturated hydrocarbon and a ketone.

The hydrocarbon, C_6H_{10}, is a colourless, mobile oil with an odour of terpin, which boils at 69° under the ordinary pressure, and forms an additive compound with 1 mol. of bromine.

The ketone, $COEtPr^{\beta}$, boils at 114° and forms an *oxime*, $C_6H_{13}ON$, which is a colourless, mobile liquid boiling at 74° under 11 mm. pressure. When boiled with acetic anhydride, the oxime forms the *acetyl* derivative, $C_6H_{12}ONAc$, which is a transparent, mobile liquid with an ester-like odour and boils at 94—96° under 14 mm. pressure. As the ketone reduces ammoniacal silver solution, it probably contains traces of methyl*iso*propylacetaldehyde, which boils at 116°.

The *dioxide*, $O<\begin{matrix}CHEt\cdot CHMe\cdot CH_2\\CH_2\cdot CHMe\cdot CHEt\end{matrix}>O$, is a yellow, mobile oil, which boils at 102° under 13 mm. or at 214° under the ordinary pressure, is insoluble in water, and does not enter into reaction with zinc ethyl at 100° or with water at 200°. G. Y.

Action of Silver Cyanate on Acyl Chlorides. IV. Methanesulphonylcarbimide. Otto C. Billeter (*Ber.*, 1905, **38**, 2013—2015. Compare Abstr., 1903, i, 821; 1904, i, 397).—When molecular amounts of silver cyanate and methanesulphonic chloride are heated at 120°, a violent action occurs with the formation of a yellow product, which does not contain cyanate and which is probably methanesulphonic anhydride. When the action was moderated, the presence of methanesulphonic anhydride (compare this vol., i, 584) in the reaction mixture was detected. The portion of the latter which distilled at 50—80° under 10 mm. pressure was again treated with silver cyanate, the lower boiling fraction again separated, and the treatment with silver cyanate repeated in this manner eight times, when *methanesulphonylcarbimide*, $CH_3\cdot SO_2\cdot N{:}CO$, was isolated. It melts at 31°, boils at 73·5—75° under 10 mm. pressure, solidifies in rhombic plates, and separates from ether in needles. It is very readily attacked by water and by alcohol. With water, it forms methanesulphonamide. A. McK.

Action of Sodium on Aliphatic Esters. Louis Bouveault and René Locquin (*Compt. rend.*, 1905, **140**, 1593—1595. Compare Abstr., 1903, i, 597, 673; 1904, i, 642, 730).—The dry aliphatic ester is added slowly and in small quantities at a time to sodium wire suspended in dry ether contained in a flask cooled by immersion in ice. When the whole of the ester has been added, the flask is withdrawn from the ice and allowed to assume the atmospheric temperature; it is then set aside until the whole of the sodium has been converted into a white or bright yellow powder.

Applying this process to ethyl butyrate, there are produced (1) butyroin, $COPr^{\alpha}\cdot CHPr^{\alpha}\cdot OH$, which boils at 95° under 20 mm. pressure, has a sp. gr. 0·9367 at 0°/4°, and is identical with that obtained by Klinger and Schmitz (Abstr., 1891, 890); (2) dibutyryl; and (3) a *substance*, produced by the condensation of 2 mols. of butyroin with the loss of a mol. of water. This is a liquid which boils at 155—157° under 12 mm. pressure and has a sp. gr. 0·9398 at 0°/4°.

Under the same conditions, ethyl hexoate yields *caproin*, $C_{12}H_{24}O_2$, a

liquid boiling at 142° under 10 mm. pressure, *dihexoyl*, which boils at 120° under 10 mm. pressure and furnishes a *dioxime* melting at 181°, and *dicaproin*, produced by the condensation of 2 mols. of caproin with the loss of a mol. of water, which boils at 215—220° under 10 mm. pressure.

It appears that this reaction may furnish a general method of preparing *a*-disecondary glycols and *s*-*a*-diketones (compare this vol., i, 572). T. A. H.

Derivatives of Normal Hexoic Acid. Louis Henry (*Bull. Acad. roy. Belg.*, 1905, 158—177).—n-*Hexonitrile*, prepared by dehydrating the corresponding amide with phosphoric oxide, is a colourless, pleasant-smelling liquid with a sweetish taste; it boils at 162—163° under 750 mm. pressure, has a sp. gr. 0·8093 at 20° and n_D 1·41154. *iso*Hexonitrile boils at 154—155°.

n-Hexyl chloride, prepared from hexyl alcohol obtained from hexoic acid by Bouveault and Blanc's process (Abstr., 1904, i, 642), boils at 134—135° under 763 mm. pressure, has a sp. gr. 0·8720 at 20° and n_D 1·4244.

n-*Hexyl mercaptan*, obtained by treating hexyl iodide with potassium hydrogen sulphide in alcohol, boils at 149—150° under 768 mm. pressure and has a sp. gr. 0·8486 at 20°. The substance described under this name by Pelouze and Cahours (*Compt. rend.*, 1862, **54**, 1241) is probably the *sec.*-hexyl mercaptan (compare Erlenmeyer and Wanklyn, Trans., 1864, **17**, 193). *n*-Amyl mercaptan boils at 126—127°.

n-*Hexyl nitrite* is a mobile, faintly yellow liquid with a pleasant odour; it boils at 129—130° under 774 mm. pressure, has a sp. gr. 0·8851 at 20° and n_D 1·40181. With methyl alcohol, it yields methyl nitrite and hexyl alcohol. n-*Nitrohexane*, obtained by the action of silver nitrite on hexyl iodide, is a colourless liquid with a faint odour and sweetish taste; it boils at 193—194° under 765 mm. or at 112° under 75 mm. pressure, and has a sp. gr. 0·9488 at 20°. The substances described under this name by Worstall (Abstr., 1899, i, 399) and Auger (Abstr., 1900, i, 578) are regarded as mixtures of normal nitro-hexane with *sec.*-nitrohexane (Konowaloff, Abstr., 1892, i, 575) and hexyl nitrite respectively.

n Heptonitrile, obtained by the action of potassium cyanide on hexyl iodide dissolved in alcohol, boils at 183—184° under 765 mm. pressure, has a sp. gr. 0·8153 at 20° and n_D 1·4195 (compare Mehlis, Abstr., 1878, 134; and Hell and Kitrosky, Abstr., 1891, 812).

The boiling points of the normal aliphatic nitriles and the corresponding alcohols are tabulated in the original and show that the change in boiling point due to the replacement of $-CN$ by $-CH_2{\cdot}OH$ in this series ranges from $-1°$ to $-8°$ except in the case of hydrocyanic acid and methyl alcohol where the change is $+40°$.

T. A. H.

Methylbutylacetic [a-Methylhexoic] Acid. P. Rasetti (*Bull. Soc. chim.*, 1905, [iii], **33**, 687—691. Compare following abstract). —*Ethyl methylbutylmalonate*, $C_4H_9{\cdot}CMe(CO_2Et)_2$, obtained by the action of normal butyl iodide on the sodium derivative of ethyl

malonate, boils at 235·5—237·5°. The *methyl ester* boils at 219—221°. The *free* acid crystallises in slender needles, melts at 99—101°, and yields crystalline *copper* and *barium* salts.

α-Methylhexoic acid, $C_4H_9\cdot CHMe\cdot CO_2H$, obtained by heating the foregoing acid at 180°, boils at 209·5—211° (compare Kiliani, Abstr., 1886, 438, 441). The *methyl ester* boils at 159—160°, and the *ethyl ester* at 174—175°. *α-Methylhexoamide* separates in small needles from water or spangles from carbon disulphide and melts at 70—72·5°. The *chloride* of the acid and the calcium salt were also prepared (compare Kiliani, *loc. cit.*). T. A. H.

Ethylpropylacetic [α-Ethylvaleric] Acid. P. Rasetti (*Bull. Soc. chim.*, 1905, [iii], **33**, 684—687).—*Ethyl ethylpropylmalonate*, $CEtPr^{\alpha}(CO_2Et)_2$, prepared by the action of ethyl bromide or iodide on the sodium derivative of ethyl propylmalonate, is a colourless oily liquid and boils at 234—236°. The *methyl ester* is similar, boils at 215—217°, has a sp. gr. 1·0335 at 0°/0° and 1·0140 at 21°/21° and n_D 1·43035 at 21°. The *acid* forms slender needles and melts at 117—118°. The *barium* and *copper* salts were prepared.

α-Ethylvaleric acid, $CHEtPr^{\alpha}\cdot CO_2H$, prepared by heating ethylpropylmalonic acid at 180°, boils at 208—209° (compare Kiliani, Abstr., 1886, 441). The *methyl ester* boils at 155—156·5°, the *ethyl ester* at 169—171°, and the *chloride* at 158—160°. *α-Ethylvaleramide* crystallises from carbon disulphide and melts at 102·5—103·5°.

T. A. H.

Synthesis of Fats. Ad. Grün (*Ber.*, 1905, **38**, 2284—2287).—αγ-Diglycerides are formed by dissolving glycerol in sulphuric acid, and warming the disulphate so obtained with the fatty acid dissolved in concentrated sulphuric acid. βγ-Diglycerides are formed in the same manner from glycerol α-chlorohydrin. The following glycerides have been prepared by this method.

αγ-Dipalmitin melts at 70°, and, when treated with an excess of acetic anhydride in pyridine solution, forms *β-acetyl-αγ-dipalmitin*, $OAc\cdot C_3H_5(O\cdot C_{16}H_{31}O)_2$, which separates from alcohol in spherical, crystalline aggregates, and melts at 49°, or after fusion and resolidification at 33°.

αγ-Distearin crystallises in white needles, sinters at 58°, and melts at 76° (m. p. 58°, Berthelot, this Journ., 1853, **6**, 283; 76·5°, Hundeshagen, Abstr., 1884, 280). αγ-Diarachin melts at 75°.

Dipalmito-α-chlorohydrin, $C_3H_5Cl(O\cdot C_{16}H_{31}O)_2$, separates from alcohol as an oil which solidifies to small, soft crystals; it melts at 48—50°, yields potassium chloride on hydrolysis with alcoholic potassium hydroxide, and when heated with silver acetate and glacial acetic acid in a sealed tube at 140°, yields *α-acetyl-βγ-dipalmitin*, which sinters at 52° and melts at 67°. A mixture of the α- and β-acetyldipalmitins commenced to melt at 49—50° and was clear at 63°.

G. Y.

Aldehydo-acids. Edmond E. Blaise and A. Courtot (*Compt. rend.*, 1905, **141**, 41—42. Compare Perkin and Sprankling, Trans., 1899, **75**, 11).—ααβ-Trimethyl-Δ^{β}-butenoic acid, $CH_2\colon CMe\cdot CMe_2\cdot CO_2H$

(m. p. 35°), when brominated, yields *aaβ-trimethyl-βγ-dibromobutyric acid* (m. p. 125°), and this, when heated, furnishes a *bromo-lactone*, $\begin{matrix} CMe_2\text{—}CO \\ CMeBr\cdot CH_2 \end{matrix}\!\!>\!O$, which, in turn, by further heating, either alone or with quinoline, yields the corresponding unsaturated *lactone*,

$$\begin{matrix} CMe_2\cdot CO \\ CMe\!:\!CH \end{matrix}\!\!>\!O,$$

and this, on hydrolysis, gave the corresponding *aldehydo-acid*, which, however, reacts as if it had the constitution $\begin{matrix} CMe_2\text{—}CO \\ OH\cdot CH\cdot CHMe \end{matrix}\!\!>\!O$; this melts at 63°, has the mol. volume 130·47 in toluene (the open chain formula requires 146·1), reacts with phenylcarbimide, forming a *phenylurethane* melting at 134°, furnishes an *acetyl* derivative, and does not give Schiff's reaction or form acetals. On the other hand, the closed chain appears to be easily opened, since the characteristic aldehyde reactions with phenylhydrazine, hydroxylamine, &c., take place.

By a similar series of reactions, *β-phenyl-aa-dimethylbutyrolactone*, having the constitution $CHPh\!<\!\begin{matrix} CMe_2\cdot CO \\ CH(OH) \end{matrix}\!>\!O$ and melting at 131°, was prepared.

T. A. H.

Ethyl Formylacetate and Ethyl α-Formylpropionate. Arthur Michael (*Ber.*, 1905, 38, 2096—2105. Compare this vol., i, 195).—Resorcinol and ethyl sodio-α-formylpropionate in absolute alcoholic solution form an additive compound, as in this the sodium is more fully neutralised than in ethyl sodio-α-formylpropionate. On expulsion of the alcohol and acidification of the reaction mixture, after three days, α-methylumbelliferone, $OH\cdot C_6H_3\!<\!\begin{matrix} O\text{—}CO \\ CH\!:\!CMe \end{matrix}$, is obtained as a gummy precipitate, which, on crystallisation from alcohol, forms white, prismatic needles, melts at 217—219°, and dissolves in aqueous alkali hydroxides to blue fluorescent solutions, from which it is precipitated unchanged on acidification.

The action of methyl iodide on ethyl sodioformylacetate in absolute alcoholic solution leads to the formation of ethyl trimesate and a small quantity of a neutral oil which boils at 69·5—70·5° under 22 mm. pressure, and is possibly a mixture of the unchanged ester and its methyl derivative, or may be derived from an impurity in the sodio-ester (see Wislicenus and Bindemann, Abstr., 1901, i, 361).

Ethyl α-formylpropionate is best formed by adding a mixture of ethyl formate and propionate to sodium under ether cooled by ice-water. After acidification and fractionation, a small, crystalline residue is obtained, which crystallises in silky leaflets and melts at 96—97°. The action of methyl iodide and sodium ethoxide on ethyl α-formylpropionate in alcoholic solution leads to the formation of a small amount of a neutral oil, which boils at 68—70° under 20 mm. pressure, and is probably impure ethyl α-formyl*iso*butyrate, as it gives the phenylhydrazine reaction for aldehydes.

Ethyl sodioformylacetate and benzenediazonium chloride react in

aqueous solution at 0° to form a brown oil which, on recrystallisation from alcohol, yields ethyl formazylcarboxylate. If the sodio-ester and diazonium chloride are rapidly mixed and immediately extracted with ether, the *phenylhydrazone* of ethyl formylglyoxylate,

$$C_{11}H_{12}O_3N_2,$$

is obtained as a viscid red oil. This is also formed by adding a cooled aqueous solution of benzenediazonium chloride to ethyl sodioformylacetate in absolute alcohol and pouring the mixture into ice-water. With phenylhydrazine in glacial acetic acid solution, it forms the *diphenylhydrazone*, $C_{17}H_{18}O_2N_4$, which crystallises in yellow prisms and melts at 215—217°. The action of benzenediazonium chloride on ethyl sodio-α-formylpropionate leads to the formation of the phenylhydrazone of ethyl pyruvate.

Ethyl sodioformylacetate and hydroxylamine hydrochloride react in cold aqueous solution to form the *oxime*, $C_5H_9O_3N$, which crystallises in long, white prisms and melts at 57—59°. The *oxime* of ethyl α-formyl propionate, $C_6H_{11}O_3N$, formed by the action of hydroxylamine on the ester in alcoholic solution, is an oil. The action of phenylhydrazine hydrochloride on ethyl α-formylpropionate in aqueous solution leads to the formation of 1-*phenyl*-4-*methyl*-5-*pyrazolone*, $C_{10}H_{10}ON_2$, which crystallises in concentric aggregates of small prisms, melts at 147—148°, and has weak acid and weak basic properties. With phenylhydrazine in ethereal solution, ethyl α-formylpropionate forms 1-phenyl-4-methyl-5-pyrazolone and an *isomeride*, which crystallises in plates and prisms and melts at 124—126°. G. Y.

Syntheses with Ethyl Sodioacetoacetate. ARTHUR MICHAEL (*Ber.*, 1905, **38**, 2083–2096. Compare Claisen and Haase, Abstr., 1901, i, 118).—The author has prepared ethyl *O*-acetylacetoacetate by the action of acetyl chloride on the copper derivative of ethyl acetoacetate (Nef, Abstr., 1893, i, 828), and by treating ethyl acetoacetate with acetyl chloride in pyridine solution (Claisen and Haase, Abstr., 1900, i, 373); the latter process gave much the better yield. Both products boiled at 99—99·5° (corr.) under 12 mm. pressure, and no difference could be detected in their chemical behaviour.

Ethyl diacetoacetate is not formed by the action of ethyl sodioacetoacetate on the *O*-acetylacetoacetate in cooled absolute ethereal solution, but is obtained as the chief product on adding ethyl sodioacetoacetate suspended in ether to an ethereal solution of acetyl chloride at −10° (compare Elion, *Rec. Trav. chim.*, 1884, **3**, 250). Contrary to Claisen's statement (Abstr., 1894, i, 31), when ethyl sodioacetoacetate and *O*-β-carbethoxyacetoacetate are heated together in ethereal solution at 100°, no diacetoacetate, but only a small amount of a neutral oil boiling at 198°, is formed, and no interaction takes place between the copper derivative of ethyl acetoacetate and ethyl *O*-β-carbethoxyacetoacetate, when these are heated together in benzene solution at 100°. The formation of ethyl sodiodiacetoacetate by the action of acetyl chloride on ethyl sodioacetoacetate must be due to primary formation of the diacetoacetate and its subsequent interaction with unchanged sodioacetoacetate, or to the formation of a complex molecule from 2 mols. of ethyl sodioacetoacetate and 1 mol. of acetyl

chloride, and its subsequent decomposition with formation of ethyl acetoacetate and sodiodiacetoacetate and sodium acetate.

A *copper* derivative, $C_{10}H_{18}O_4Cu$, is formed by the action of cuprous chloride on ethyl sodioethylacetoacetate in absolute alcoholic solution (compare Wedel, Abstr., 1884, 834). It is a green powder which decomposes at 100°, or when quickly heated melts with effervescence at 188—189°, is insoluble in the ordinary solvents and is decomposed by warm water. When dried and treated with acetyl chloride in ethereal solution, the copper derivative yields a small amount of an oil which boils at 123° under 20 mm. pressure, and is identical with Elion's product from the action of acetyl chloride on ethyl sodioethylacetoacetate (*loc. cit.*).

When warmed with mercuric oxide, with or without ether, ethyl acetoacetate forms the crystalline mercuric derivative, $(C_6H_9O_3)_2Hg_2$, which is stable towards water or dilute acids, and is probably identical with Lippmann's compound (*Zeit. Chem.*, 1869, **12**, 29).

In the preparation of ethyl alkylacetoacetates by the action of alkyl iodides on ethyl sodioacetoacetate, the unchanged acetoacetate is best removed by shaking the ethereal solution with dilute ammonia (compare Brühl, Abstr., 1904, i, 139). Three methods for the purification of alkylacetoacetates are described.

(1) The ester is stirred into a concentrated aqueous solution of potassium hydroxide cooled by ice-water, ether added, and the precipitate of ethyl potassioalkylacetoacetate filtered and washed with ether; the dialkylacetoacetate present is obtained by fractionation of the ethereal filtrate and washings, and the alkylacetoacetate by treatment of the precipitate with hydrochloric acid and fractionation of the liberated oil.

(2) The ester, dissolved in ether, is converted by sodium into the sodio-derivative and shaken with slightly less than 1 mol. of water; the insoluble hydrate formed in this manner is filtered, washed with ether, and decomposed by ice-cooled, dilute hydrochloric acid.

(3) The ester is treated with 1 mol. of sodium ethoxide dissolved in alcohol and with an alcoholic solution of cupric chloride until the precipitation is complete. The copper derivative, after being washed with alcohol and ice-water, is mixed with ice and decomposed by concentrated hydrochloric acid.

Of these methods, the first is the most easily carried out, but the second gives the best yields. Owing to hydrolysis of the ester, the purification is always accompanied by considerable loss of material (compare Wislicenus, Abstr., 1878, 402).

Ethyl dimethylacetoacetate is purified by shaking, and ethyl diethylacetoacetate, which is more stable, by boiling, with a 25 per cent. solution of potassium hydroxide. G. Y.

Action of Methyl and Ethyl Chloro-oxalates on Acetylacetone. R. TRIMBACH (*Bull. Soc. chim.*, 1905, [iii]. **33**, 693—695. Compare this vol., i, 323).—When methyl chloro-oxalate is added to the copper derivative of acetylacetone, dissolved in chloroform, *methyl acetylacetonyloxalate*, $CHAc_2\cdot CO\cdot CO_2Me$, is formed, and may be obtained as an oil by filtration and subsequent removal of the solvent

by distillation. This oil crystallises after a long time (a year was necessary in the initial preparation), but a more rapid separation of crystals may be induced by sowing the oil with the crystalline substance prepared previously. It crystallises in almost colourless needles or prisms, melts at 69°, and is readily soluble in alcohol or ether, less so in benzene. The solution in methyl alcohol attacks metallic copper, producing a green, crystalline substance. Water converts the ester into acetylacetone and oxalic acid. With phenylhydrazine, a *substance* is obtained which crystallises from boiling pyridine in colourless, silky needles, decomposes at 245° without melting, and may be sublimed. The *product* formed by the action of ethyl chloro-oxalate on acetylacetone is an uncrystallisable oil.

T. A. H.

Derivatives of Azelaic Acid. A. BOUCHONNET (*Compt. rend.*, 1905, **140**, 1599—1601. Compare Etaix, Abstr., 1898, i, 124; Derlon, Abstr., 1898, i, 638; Miller, Abstr., 1899, i, 789, 791).—*Phenyl azelate*, $C_7H_{14}(CO_2Ph)_2$, prepared by the action of azelayl chloride on phenol, forms flocculent masses of white needles, melts at 48—49°, and is slightly soluble in cold alcohol, readily so in ether, benzene, or carbon disulphide.

Thioazelaic acid, $C_7H_{14}(CO{\cdot}SH)_2$, obtained by heating phenyl azelate with sodium hydrogen sulphite in alcohol, forms bright yellow needles, melts at 72—74°, and is very soluble in ether, benzene, or alcohol. The *sodium* salt is very soluble in water. On adding lead acetate to an aqueous solution of the acid or the sodium salt, a yellowish-white precipitate, which rapidly becomes brown and then black, is produced. A similar reaction takes place with thiosuccinic acid. T. A. H.

Synthesis of the Lactone of Erythric Acid. ROBERT LESPIEAU (*Compt. rend.*, 1905, **141**, 42—43. Compare Abstr., 1904, i, 471).—By boiling $\beta\gamma$-dichlorobutyric acid with an aqueous solution of potassium carbonate, hydroxycrotonolactone, $\begin{matrix}CH{\cdot}CH_2\\ \| \\ CH{-}CO\end{matrix}\!\!>\!O$, is produced (*loc. cit.*), and this, on oxidation with barium permanganate, furnishes *erythrolactone*, $\begin{matrix}OH{\cdot}CH{\cdot}CH_2\\ | \\ OH{\cdot}CH{-}CO\end{matrix}\!\!>\!O$. This crystallises from acetone in monoclinic prisms and from benzene in needles, melts at 91°, and is soluble in water, less so in alcohol or ether. T. A. H.

New Form of Thallium Tartrate. Isomorphous Mixtures of Thallium and Potassium Tartrates. JEAN HERBETTE (*Compt. rend.*, 1905, **140**, 1649—1652).—When a concentrated solution of thallium tartrate is induced to crystallise by the addition of a crystal of potassium tartrate, monoclinic crystals of a variety of hydrated thallium tartrate, $[Tl_2C_4H_4O_6]_2,H_2O$, are deposited. It is proposed to distinguish this as the *M* form. The crystals closely resemble those of potassium tartrate, and have $[a:b:c = 3{\cdot}1056:1:3{\cdot}9407;\ \beta = 90°]$.

The properties of the mixed crystals obtained by starting crystallisation in solutions of thallium tartrate of various concentrations

with potassium tartrate do not vary proportionally with the chemical composition; thus the angle β has the value 90° in thallium tartrate (72·2 per cent. of thallium), and falls to 88°36′ in mixed crystals containing from 49·7 to 54·0 per cent. of thallium, and rises again to 89°10′ in potassium tartrate. These mixed crystals are always richer in thallium than the solutions from which they separate. No crystals having the composition of a double salt were obtained. T. A. H.

Cysteine. II. CARL NEUBERG and PAUL MAYER (*Zeit. physiol. Chem.*, 1905, **44**, 472—497. Compare Abstr., 1902, i, 743; Friedmann, *ibid.*, 731; 1903, i, 75, 301; E. Erlenmeyer, jun., *ibid.*, 1903, i, 791; this vol., i, 120; Gabriel, this vol., i, 266).—Two structurally isomeric cystines occur in nature, and these are termed *protein-cystine* and *calculus-cystine*, although urinary calculi often consist of a mixture of the two. Friedmann's cystine is pure protein-cystine; it crystallises in six-sided plates, has no definite melting point, but decomposes slowly at 258—261°, and it has $[\alpha]_D - 224°$; its phenylcarbimide (Patten, Abstr., 1903, i, 792) melts at 160° (corr.), and when boiled with 25 per cent. hydrochloric acid yields an anhydride melting at 119° (corr.). Protein-cystine does not give Bamberger's hydroxamic acid test, but on treatment with nitrous acid yields the disulphide of β-thioglyceric acid. The benzoyl derivative (Brenzinger, Abstr., 1892, 1111) melts at 182—184° (corr.), the mercuric derivative has the composition $Hg[CO_2{\cdot}CH(NH_2){\cdot}CH_2]_2S_2$, and is quite stable. Protein-cystine yields an *S*-ethylcysteine,

$$SEt{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H,$$

which melts at 228—230°, and a corresponding *benzyl* derivative melting at 226—228° (compare Brenzinger; Suter, Abstr., 1895, i, 624). Racemic protein-cystine crystallises in groups of needles resembling tyrosine, and the cysteine obtained by the reduction of protein-cystine yields a mercurichloride represented by the formula

$$[SHgCl{\cdot}CH_2{\cdot}CH(NH_2HCl){\cdot}CO_2H]_2,HgCl_2.$$

Calculus-cystine crystallises in needles, melts and decomposes at 190—192°, is more readily soluble than its isomeride, and in hydrochloric acid solution has $[\alpha]_D - 206°$. Its *phenylcarbimide* melts at 170—172° (corr.), and seems not to be decomposed when boiled with hydrochloric acid. Calculus-cystine gives Bamberger's hydroxamic acid test, and with nitrous acid undergoes complex decomposition. The *benzoyl* derivative melts at 157—159° (corr.), the mercuric derivative decomposes when dried, and has no definite composition. The *ethyl* derivative of calculus-cysteine melts at 164—166°, and the *benzyl* derivative at 213°. *Racemic* calculus-cystine is amorphous, and the cysteine obtained on reducing calculus-cystine yields a mercurichloride,

$$NH_2{\cdot}CH_2{\cdot}CH{<}{}^{S—}_{CO_2}{>}Hg,HgCl_2.$$

Although calculus-cystine resembles Gabriel's inactive *iso*cystine, it is not certain that the two are identical.

The active protein- and calculus-cystines yield mixed crystals in the form of definite needles, which appear quite homogeneous. When heated with hydrochloric acid at 165°, both compounds are racemised.
J. J. S.

d-, l-, and r-Protein-cystines. CARL NEUBERG and PAUL MAYER (*Zeit. physiol. Chem.*, 1905, **44**, 498—510. Compare preceding abstract, and Mauthner, Abstr., 1902, i, 133).—The sodium derivative of natural protein-cystine, $S_2[CH_2\cdot CH(NH_2)\cdot CO_2Na]_2$, is readily obtained by dissolving cystine in the requisite amount of N-sodium hydroxide, and on addition of certain metallic salts precipitates are obtained. The following have been analysed: *silver*, $C_6H_{10}O_4N_2S_2Ag_2$, *mercuric*, *lead*, *cadmium*, and *copper*, $C_6H_{10}O_4N_2S_2Cu$.

Mercuric acetate is a much better precipitant for cystine than either the sulphate or chloride.

A 50 per cent. yield of r-cystine is obtained when the natural product is heated with 15—20 times its weight of hydrochloric acid of sp. gr. 1·124 at 165° for 12—15 hours. It decomposes at the same temperature as the active compound, but is almost three times as soluble in water. The acid thus obtained is mainly the racemic and not the *meso*-form, since it can be resolved into active components by means of *Aspergillus niger*, the d-compound being left.

A r-cysteine has been obtained by reducing r-cystine. J. J. S.

Crystalline Form of Sodium Formaldehydesulphoxylate (Rongalit C.); A. OSANN (*Ber.*, 1905, **38**, 2290—2291. Compare Baumann, Thesmar, and Frossard, this vol., i, 260; Reinking, Dehnel, and Labhardt, this vol., i, 261; Bazlen, this vol., ii, 240).—Sodium formaldehydesulphoxylate dissolves in twice its weight of cold water; it crystallises in transparent, rhombo-holohedral plates [$a:b:c=0·8421:1:0·6783$], which are easily obtained weighing as much as 400 grams. G. Y.

Aldehyde-ammonia. PAUL DUDEN, K. BOCK, and H. J. REID (*Ber.*, 1905, **38**, 2036—2044. Compare this vol., i, 558).—*Potassium β-amino-α-*aci-*dinitropropane*, $NH_2\cdot CHMe\cdot C(NO_2)\colon NO_2K$, prepared by the action of aldehyde-ammonia on potassium *aci*-dinitromethane, forms yellow crystals and decomposes at about 120°; acetaldehyde is evolved when its aqueous solution is boiled. The condensation is represented by the equation $NH_2\cdot CHMe\cdot OH + NO_2\cdot CH\colon NO_2K = H_2O + NH_2\cdot CHMe\cdot C(NO_2)\colon NO_2K$.

*α-Piperidyl-β-*aci-*dinitroethane*, $C_5NH_{10}\cdot CH_2\cdot C(NO_2)\colon NO_2H$, prepared from dinitromethane and 1-hydroxymethylpiperidine, separates from water in glistening needles and is stable when boiled with acids or alkalis. Its *acetyl* derivative forms colourless needles, which become green on exposure to air. Piperidyl-*aci*-dinitroethane is readily reduced by stannous chloride.

*α-Methylamino-β-*aci-*dinitroethane*, $C_3H_7O_4N_3$, separates from water in glistening plates and melts at 126—127°. *α Dimethylamino-β-*aci-*dinitroethane*, $C_4H_9O_4N_3$, separates from water in hexagonal plates and melts at 115—117°.

Tetramethyldiaminonitropropane, $NO_2\cdot CH(CH_2\cdot NMe_2)_2$, prepared from acetaldehyde and hydroxymethyldimethylamine, melts at 58°. On exposure in a vacuum desiccator, it is quickly converted into a brown tar; its *hydrochloride* and *sodium* salt were prepared. Its aqueous solution is readily decomposed on boiling. When a solution of aniline in water

is added to its aqueous solution at 60—70°, *αγ-dianilino-β-nitropropane*, $NO_2\cdot CH(CH_2\cdot NHPh)_2$, separates in yellow, quadratic leaflets, and melts at 157°. It is only slightly basic and is decomposed by acids or by alkalis much more slowly than is tetramethyldiaminonitropropane. Its *acetyl* derivative, $NO_2\cdot CH(CH_2\cdot NPhAc)_2$, prepared by boiling with acetic anhydride, crystallises in prisms and melts at 129°. When dilute sulphuric acid is added to the solution of this diacetyl compound in an aqueous solution of sodium hydroxide, the *isomeric acetyl* derivative, $C(CH_2\cdot NPhAc))_2\colon NO_2H$, is precipitated; it gives a coloration with ferric chloride and is readily transformed into the former variety.

αγ-Tetramethyldiamino-β-aminopropane, $NH_2\cdot CH(CH_2\cdot NMe_2)_2$, prepared by the reduction of a solution of tetramethyldiaminonitropropane in hydrochloric acid by stannous chloride, is a yellowish oil which boils at 174—175°.

*α-Piperidyl-β-*iso*nitrosophenylethylketone*,

$$C_5NH_{10}\cdot CH_2\cdot C(\colon NOH)\cdot COPh,$$

prepared by the action of *iso*nitrosoacetophenone (1 mol.) on *N*-hydroxymethylpiperidine (1 mol.), crystallises in hexagonal plates, and melts and decomposes at 134—135°. The *compound* $C_{15}H_{27}O_2N_3$, prepared by the interaction of *iso*nitrosoacetophenone, formaldehyde (2 mols.), and piperidine (2 mols.), separates from alcohol in red crystals and melts at 165°. It is probably the piperinomethyl ether of α-piperidyl-β-*iso*nitroso-γ-*aci*-butanone,

$$C_5NH_{10}\cdot CH_2\cdot C(\colon NOH)\cdot C(\colon CH_2)\cdot O\cdot CH_2\cdot C_5NH_{10}.$$

A. McK.

Bromination of Paraldehyde. PAUL FREUNDLER (*Compt rend.*, 1905, **140**, 1693—1694).—Bromoacetaldehyde is readily obtained when paraldehyde is treated with bromine at −5° to 0°. It is not possible to introduce a second atom of bromine by operating at this temperature. If after addition of a second molecule of bromine the mass is allowed to become warm and is then poured into a mixture of ice and sodium carbonate solution, crystals of *tetrabromobutaldehyde*,

$$CH_2Br\cdot CHBr\cdot CBr_2\cdot CHO,$$

separate; this crystallises in large prisms, melts at 63—64°, boils at 145—147° under 13 mm. pressure, and is insoluble in water, but can be readily crystallised from ether or acetone. Tetrabromobutaldehyde is also formed when bromoacetaldehyde is treated successively with sulphuric acid and bromine, reaction taking place according to the equations $2CH_2Br\cdot CHO = CH_2Br\cdot CH\colon CBr\cdot CHO + H_2O$; $CH_2Br\cdot CH\colon CBr\cdot CHO + Br_2 = CH_2Br\cdot CHBr\cdot CBr_2\cdot CHO$. It exhibits anomalous behaviour; it does not yield a hydrate, or a semicarbazone, or a bisulphite compound; it is not sensibly acted on by phosphorus pentabromide at 100°, or by concentrated aqueous alkali solutions. When warmed with ethyl alcohol, it decomposes completely, ethyl bromide, bromoacetaldehyde, bromoacetal, and probably ethyl bromoacetate being produced. Fuming nitric acid oxidises it in the cold with the formation of bromoacetic acid and hydrogen bromide. In ethereal solution, it is acted on by magnesium and some butaldehyde is formed. Crotonaldehyde is obtained from it by the action of zinc

and boiling water. When intimately mixed with large excess of sodium hydroxide and heated in a vacuum, a mixture of ethylene and acetylene bromides distils over; amongst these the bromide

$CH_2Br\cdot C\vdots CBr$

was recognised. The residue contains formic acid. H. M. D.

Crystals of *s*-Tetrachloro*iso*propyl Formal. GIUSEPPE CESÀRO (*Bull. Acad. roy. Belg.*, 1905, 128—129).—The author indicates that an error has been made in the determination of at least one of the crystallographic constants of this substance (Stappers, this vol., i, 261), and suggests that a re-examination of the crystals should be made.

T. A. H.

Preparation of Acraldehyde by the Boric Acid Method. GEORG LOCKEMANN and OTTO LIESCHE (*J. pr. Chem.*, 1905, [ii], **71**, 474—496. Compare Wohl and Neuberg, Abstr., 1899, i, 565).—The authors describe and figure the apparatus used by them in the preparation of acraldehyde by Wohl and Neuberg's method, and in the fractional distillation of the products. With 1·5 kilos. of glycerol of sp. gr. 1·245, and 1 kilo. of boric acid, the yield of crude product amounts to 30—40 per cent. of the theoretical. After repeated distillation, a fraction is obtained boiling at 22—24°, consisting of acetaldehyde and representing 6—9 per cent. of the product, about 4—5 per cent. of which is obtained as fractions of high boiling point, containing substances of the nature of guaiacol and cresol. A fraction boiling at 26—27° contains, along with acetaldehyde, a substance which separates in slender, spear-like crystals, partially sublimes and partially melts at 60—65°, and may be metacraldehyde.

The gases evolved in the preparation of acraldehyde by this method consist of 48·6 per cent. of carbon monoxide, 13·9 of methane, 13·2 of hydrogen, 6·3 of oxygen, and 18·0 of nitrogen.

Contrary to Wohl and Neuberg's statement (*loc. cit.*), the polymerisation of acraldehyde is retarded by the presence of acetaldehyde, and takes place the more readily the greater the degree of purification. The polymerisation products are insoluble in cold 10 per cent. hydrochloric acid, and consist to the extent of 95 per cent. of disacryl resin, which is insoluble in cold alcohol, the remaining 5 per cent. consisting of hexacrolic acid.

Whilst the preparation of the acraldehyde by Wohl and Neuberg's method is accompanied by the formation of so many bye-products, no acetaldehyde is formed when glycerol is heated with potassium hydrogen sulphate, and, with the exception of sulphur dioxide, there are only traces of bye-products. G. Y.

New β-Ketonic Aldehydes. FRANÇOIS COUTURIER and G. VIGNON (*Compt. rend.*, 1905, **140**, 1695—1697).—A number of β-ketonic aldehydes of the type $R\cdot CO\cdot CH_2\cdot CHO$ or $R\cdot CO\cdot CH\colon CH\cdot OH$ have been prepared by acting on a mixture of ethyl formate and a ketone with metallic sodium. The copper salts of the ketonic aldehydes, prepared by treating solutions of the sodium salts with acetic acid and copper acetate, were purified by crystallisation from ether. From

these the free aldehydes were obtained by the action of dilute sulphuric acid.

Diethylacetoacetaldehyde, $CHEt_2.CO\cdot CH\colon CH\cdot OH$, is obtained from *as*-diethylacetone. The copper salt forms very dark blue crystals which melt at 68°. The free aldehyde boils at 60—62° under 13 mm. or at 173—174° under 760 mm. pressure without decomposing. The *semicarbazone* forms slender, white needles, which crystallise readily from absolute methyl alcohol and melt at 162°.

Trimethylacetoacetaldehyde, $CMe_3\cdot CO\cdot CH\colon CH\cdot OH$, is obtained from pinacoline. The copper salt crystallises in beautiful blue tablets which melt at 125—126°. The free aldehyde boils at 53—54° under 13 mm. or at 148° under 760 mm. pressure without decomposing, reduces alkaline copper and silver solutions, and gives a red coloration with ferric chloride.

iso*Propylacetoacetaldehyde*, $CH_2Pr^{\beta}\cdot CO\cdot CH\colon CH\cdot OH$, is obtained from methyl *iso*butyl ketone. The copper salt crystallises in blue needles which melt at 142—143°. The free aldehyde boils at 51—53° under 13 mm. pressure without decomposition, decomposes when distilled under ordinary pressure, and is unstable at the ordinary temperature, gradually turns yellow and drops of water separate out from the liquid, indicating that condensation takes place.

iso*Butylacetoacetaldehyde*, $CH_2Pr^{\beta}\cdot CH_2\cdot CO\cdot CH\colon CH\cdot OH$, is obtained from methyl *iso*amyl ketone. The copper salt melts at 120°. When this is decomposed with sulphuric acid, a red liquid is obtained which cannot be distilled even under reduced pressure without considerable decomposition. A small fraction of colourless liquid, which appears to be the free aldehyde, collects at 67—70° under 13 mm. pressure.

In reference to the stability of these ketonic aldehydes, it appears that if a side-chain is attached to the carbon atom next to the ketone group the aldehydes are stable, but the stability rapidly diminishes if CH_2 groups are interposed between the ketone group and the ramification. H. M. D.

Hydrogenation of Aldoximes. AUGUSTE MAILHE (*Compt. rend.*, 1905, **140**, 1691—1693).—The aldoximes are reduced by free hydrogen at 180—220° in presence of finely divided nickel. Primary amines are first formed according to the equation $R\cdot CH\colon NOH + 2H_2 = R\cdot CH_2\cdot NH_2 + H_2O$. Under the influence of the nickel, the primary amines are, however, converted into secondary amines according to the equation $2RCH_2\cdot NH_2 = NH(CH_2R)_2 + NH_3$. In some cases, small quantities of tertiary amines are also formed. Finely divided copper has a similar action to nickel. When reduced at 150—200°, acetaldoxime yields a considerable quantity of diethylamine and a small quantity of triethylamine.

When reduced at 210—220°, heptaldoxime yields primary, secondary, and tertiary heptylamines in the ratio 13 : 6 : 1. Heptylamine is a colourless liquid boiling at 153°; with phenylcarbimide it yields phenylheptylcarbamide, which crystallises in prismatic needles melting at 63°. Diheptylamine forms colourless needles which melt at 30°; it boils at 271° under 750 mm. pressure, is only slightly soluble in water, and yields a chloride and a carbonate which are both

deliquescent. Triheptylamine boils at 330° under 762 mm. pressure.

When the vapour of benzaldoxime is led by means of a current of hydrogen over finely divided copper at 220—230°, benzaldehyde is the chief product, but benzylamine, dibenzylamine, and tribenzylamine are also obtained. Under the influence of the heated copper, the benzaldoxime gives rise to benzaldehyde, water, and benzonitrile, and the amines are then produced by hydrogenation of the nitrile. When nickel is used instead of copper, toluene is the only reduction product obtained from benzaldoxime. H. M. D.

Electrolysis in Acetone and in Pyridine. Mario G. Levi and M. Voghera (*Gazzetta*, 1905, **35**, i, 277—290).—Electrolysis of an acetone solution of potassium thiocyanate between platinum electrodes yields, on the cathode, a whitish, crystalline crust, consisting of the potassium derivative of acetone, $CH_3\cdot CO\cdot CH_2K$, and, on the anode, a yellow, flocculent substance, having a disagreeable odour, and probably formed by the oxidation of the thiocyanate ion.

Solutions of potassium, sodium, and ammonium iodides in acetone yield, on electrolysis, iodine at the anode, and, with potassium and sodium iodides, metallic derivatives of acetone, similar to that obtained with potassium thiocyanate at the cathode, whilst with ammonium iodide there is abundant evolution of gas at the cathode.

In the electrolysis of a pyridine solution of potassium thiocyanate, using an anode of porous carbon and a cathode of nickel, a black precipitate is formed at the anode, whilst at the cathode hydrogen is evolved, and a brownish-green, explosive substance deposited which dissolves in water without evolution of gas, giving a strongly alkaline solution, and consists probably of a potassium derivative of pyridine. T. H. P.

Formation of Acetol [Acetylcarbinol] and Pyruvic Acid by Direct Oxidation of Acetone. Pastureau (*Compt. rend.*, 1905, **140**, 1591—1593).—When acetone is added to a solution of hydrogen peroxide (2 per cent.) in water, in presence of sulphuric or nitric acid, there are formed Baeyer and Villiger's acetone peroxide, $(C_3H_6O_2)_2$ (Abstr., 1900, i, 133), acetylcarbinol, and pyruvic acid. Acetone peroxide melts at 131·5°, is reduced by zinc or iron in presence of sodium hydroxide to acetone, and is also reconverted into the latter when heated with dilute sulphuric acid at 100° in closed tubes. When brominated, it yields a mixture of tetrabromoacetone and pentabromoacetone.

Similar products are formed by the action of sulphuric acid and hydrogen peroxide on other ketones. T. A. H.

Derivatives of Butyroin and Hexonoin. Louis Bouveault and René Locquin (*Compt. rend.*, 1905, **140**, 1699—1700. Compare this vol., i, 560).—It is shown that butyroin and hexonoin have both alcoholic and ketonic functions. Butyroin forms an *oxime* boiling at 143° under 10 mm. pressure and a *semicarbazone* melting at 147° (corr.). It yields a *pyruvate* which boils at 134—138° under 12 mm. pressure, the *semi-*

carbazone of which melts at 147° (corr.). Hexonoin yields a *semicarbazone* melting at 92°. When dehydrogenated by Sabatier and Senderens' method, butyroin and hexonoin yield respectively the α-diketones, dibutyryl, and dihexoyl. Dibutyryl is a yellow liquid which boils at 168° under 760° mm. pressure, and yields a *dioxime* melting at 187° (corr.).

Dihexoyl boils at 110—115° under 15 mm. pressure, and yields a *dioxime* melting at 186° (corr.). When reduced by sodium in alcoholic solution, the diketones each yield a mixture of two isomeric symmetrical glycols.

α-Octane-δε-diol is a liquid which boils at 115—120° under 10 mm. pressure. *β-Octane-δε-diol* is crystalline, and melts at 125° (corr.). Both modifications are transformed into δ-octanone by heating in a sealed tube with dilute sulphuric acid at 180°.

α-Dodecane-ζη-diol melts at 54° and boils at 155—160° under 10 mm. pressure. *β-Dodecane-ζη-diol* melts at 135—136° (corr.). Both forms yield ζ-dodecanone under the influence of dilute sulphuric acid at 200°.

In addition to these glycols, univalent secondary alcohols are formed in the reduction of the diketones by means of sodium in alcoholic solution according to the equation

$$R\cdot CO\cdot CHR\cdot OH + 4H = R\cdot CH_2\cdot CHR\cdot OH + H_2O.$$

δ-Octanol is a mobile liquid with a pleasant odour which boils at 71° under 10 mm. pressure. It yields a *pyruvate* which boils at 108—110° under 10 mm. pressure, the *semicarbazone* of which melts at 96°. When oxidised with chromic acid, it yields δ-octanone, which boils at 165—168° under 760 mm. pressure and yields a *semicarbazone* melting at 100—101°.

ζ-Dodecanol is crystalline, melts at 30°, and boils at 119° under 9 mm. pressure. Its *pyruvate* boils at 150—152° under 10 mm. pressure and yields a *semicarbazone* melting at 93—94°. When oxidised by chromic acid, *ζ-dodecanone* is formed which melts at 9°, boils at 112° under 9 mm. pressure, and yields a liquid *semicarbazone* and an *oxime* which boils without decomposing at 147° under 10 mm. pressure.

H. M. D.

Isomeric Changes of some Dextrose Derivatives, and the Mutarotation of the Sugars. Coenraad L. Jungius (*Zeit. physikal. Chem.*, 1905, **52**, 97—108).—The bulk of this paper has already been reported (Abstr., 1903, i, 733; 1904, i, 651).—Dynamical experiments on the transformation of α- and β-methyl glucosides cannot settle the question whether the transformation is direct or indirect. Similar experiments with the two methyl galactosides in methyl alcohol containing hydrogen chloride show that for a given acid concentration the transformation of the methyl galactosides is 6—7 times as rapid as that of the methyl glucosides.

The author discusses the phenomena of mutarotation, and believes it to be conditioned by a transformation in which two stereoisomerides are concerned. Sometimes, as in the cases of dextrose and lactose, this transformation may be accompanied by hydration or dehydration, but in all cases the stereoisomeric change is the essential feature.

J. C. P.

Analogy between Starch coagulated by Amylocoagulase and Pea Starch. AUGUSTE FERNBACH and JULES WOLFF (*Compt. rend.*, 1905, **140**, 1547—1549. Compare this vol., i, 312).—Pea starch when boiled with water does not form a paste, but 82—83 per cent. dissolves, and can be saccharified at 70°; about 22 per cent. is only soluble between 100° and 150°, and has properties closely analogous to those of amylocellulose or coagulated potato starch; it resists saccharification (compare Roux, this vol., i, 328), dissolves in potassium hydroxide, and the neutral solution gives an intense blue colour with iodine. Amylocoagulase is present both in the seed and pod of the green pea, and if potato starch paste is coagulated by malt extract or by pea extract, a quantity varying from 15·8 to 43·4 per cent. is converted into amylocellulose. M. A. W.

Acetylcelluloses. CARL HAEUSSERMANN (*Chem. Zeit.*, 1905, **29**, 667. Compare Abstr., 1904, i, 144, 476).—Unlike penta-acetyl cellulose (Cross and Bevan, Trans., 1890, **57**, 2), the acetyl derivatives of hydrolysed cellulose obtained from Chemische Fabrik Sulzbach (D.R.-P. 118538 and 120713) are converted into nitric acid esters when treated at the ordinary temperature with nitric acid of sp. gr. 1·52. These esters may be denitrated by warming with an aqueous solution of sodium hydrosulphide, giving rise to a hydrocellulose, the identity of which is not yet completely established. Cellit, obtained from Bayer and Co., yields, on nitration, similar compounds though in much smaller quantity. P. H.

Estimation of Methoxyl Groups in some Lignocelluloses. ALWIN S. WHEELER (*Ber.*, 1905, **38**, 2168—2169).—Methoxyl has been determined by Zeisel's method in the wood of 15 trees indigenous to North Carolina: they contained about 2·39 per cent. E. F. A.

Nitrogen in Gums. ALVISO B. STEVENS (*Amer. J. Pharm.*, 1905, **77**, 255—260).—It is shown that all gums contain nitrogen, either in combination or in intimate association. This nitrogen cannot be converted into cyanogen by the usual reaction, but pyrrole or a pyrrole derivative is obtained when a gum is heated with potassium hydroxide. The true soluble gums possess in a varying degree the properties of enzymes, the activity of the enzyme being in proportion to the amount of nitrogen present in the gum. If enzymes and gums be two distinct substances, there is at present no known method of separating them. Since the gums or the acids prepared from them cannot be obtained entirely free from nitrogen, it follows that previous elementary analyses need revision, but it is possible that in some cases the amount of nitrogen present may have been too small to materially affect the relation of carbon, hydrogen, and oxygen. W. P. S.

Iodomercurates and Chloroiodomercurate of Monomethylamine. MAURICE FRANÇOIS (*Compt. rend.*, 1905, **140**, 1697—1698). —The iodide NH_3MeI,HgI_2 separates in yellow needles from concentrated solutions containing mercuric iodide and methylammonium iodide in the molecular ratio 2 : 3. It melts at 173°, is

soluble in absolute alcohol or ether, very soluble in glacial acetic acid, but insoluble in chloroform, and is decomposed by water with separation of mercuric iodide. When heated, it undergoes decomposition into the component iodides.

The iodide $2NH_3MeI,HgI_2$ separates in large, yellow tablets when a hot concentrated solution containing mercuric iodide and methylammonium iodide in the molecular ratio 1 : 2 is allowed to cool. It melts at 221°, is insoluble in chloroform and ether, but dissolves in absolute alcohol, and is very soluble in warm acetic acid and in water.

The mixed haloid $2NH_3MeCl,HgI_2$ separates in colourless, well-formed, nacreous crystals from concentrated solutions containing mercuric iodide and methylammonium chloride in the molecular ratio 1 : 6. It melts at 139°, is soluble in absolute alcohol or acetic acid, but not in ether or in chloroform, and is decomposed by water with separation of mercuric iodide. H. M. D.

Additive Compounds of Tertiary Amines. Arthur Hantzsch and Wilhelm Graf (*Ber.*, 1905, **38**, 2154—2161).—The compound obtained by the addition of hydrogen chloride to trimethylamine oxide cannot have the oxonium constitution $NMe_3\dot{:}OHCl$, suggested by Willstätter and Iglauer (Abstr., 1900, i, 458), since aqueous solutions of the salts are only very slightly hydrolysed, and solutions of the oxide in water have a distinctly alkaline reaction. Both these properties are characteristic of ammonium rather than of oxonium derivatives, and the old formula for the salt, namely, $OH\cdot NMe_3Cl$, is retained. Since, however, this salt is not identical with the unstable hypothetical additive product of trimethylamine and hypochlorous acid (Willstätter), it is suggested that the two are isomeric, and that the trimethylamine oxide hydrochloride is trimethylhydroxyammonium chloride, $[NMe_3OH]Cl$, and the additive compound of hypochlorous acid and trimethylamine is trimethylchloroammonium hydroxide, $[NMe_3Cl]OH$. The primary product of the action of hypochlorous acid on trimethylamine is the hypochlorite of the base (as ions $NMe_3H^{\cdot}$ and OCl'), and the formation of such a salt is in harmony with the considerable increase in the electrical conductivity which is observed when the two solutions are mixed. In the decomposition of the hypochlorite to form dimethylchloroamine, a certain amount of hydrogen chloride is also formed.

Trimethylamine dibromide (Remsen and Norris, Abstr., 1896, i, 336) is readily obtained by mixing together the components in carbon disulphide solution, and crystallises from glacial acetic acid in reddish-yellow plates; it melts at 85—86° to a brownish-yellow liquid, decomposes at 170°, and is also rapidly decomposed by moisture; it is insoluble in ether, carbon disulphide, or light petroleum, and dissolves sparingly in benzene or toluene. It readily liberates two equivalents of iodine from potassium iodide solution, and hence cannot have the formula given by Norris (Abstr., 1899, i, 663). No dibromide could be obtained from dimethylaniline, as even at −40° the bromine replaces the hydrogen in the para-position. *p-Bromodimethylaniline dibromide*, $C_6H_4Br\cdot NMe_2,Br_2$, obtained from its components in

chloroform solution at low temperatures, crystallises in yellowish-red needles, melts and decomposes at about 100°, and is readily decomposed by water, alcohol, or concentrated sulphuric acid. The dibromides react with alkalis, yielding the free base, the alkali bromide, and hypobromous acid, and this can react with the base producing a bromoamide. J. J. S.

Constitution of Ammonium Salts. ARTHUR HANTZSCH (*Ber.*, 1905, **38**, 2161—2164).—The fact that alkalis do not transform trimethylamine dibromide and similar dibromides into hydroxybromides and oxides of tertiary bases, for example,

$$NMe_3Br_2 \longrightarrow NMe_3{<}^{Br}_{OH} \longrightarrow NMe_3{:}O,$$

is used as an argument against the ordinary ammonium formula (quinquevalent nitrogen) for these and other ammonium compounds, and Werner's conceptions of the constitution are accepted, namely, a quadrivalent nitrogen atom, and the acid radicle being "extra radicle" and probably within the sphere of influence of the four groups attached to the nitrogen. Trimethylammonium chloride is written $[NHMe_3]Cl$, and the dibromide of trimethylamine $[NBrMe_3]Br$. The decomposition with alkalis is then analogous to the decomposition of alkyl ammonium salts by alkali.

$$[NMe_3H]Br \longrightarrow [NMe_3H]OH \longrightarrow NMe_3 + H_2O.$$
$$[NMe_3Br]Br \longrightarrow [NMe_3Br]OH \longrightarrow NMe_3 + HBrO.$$

The compounds trimethylhydroxyammonium bromide, $[NMe_3OH]Br$, and trimethylbromoammonium hydroxide, $[NMe_3Br]OH$, are termed coordination isomerides. A third isomeride is trimethylammonium hypobromite, $[NMe_3H]OBr$, which only exists in the form of its ions in solution. The action of hypochlorous acid on trimethylamine is supposed to consist partly in the addition of the ions $Cl^{\cdot}$ and OH', and the formation of $[NMe_2Cl]OH$, which, like all ammonium hydroxides, readily decomposes partly into NMe_3 and $HClO$ and partly into NMe_2Cl and CH_3OH. (Compare Willstätter and preceding abstract.) J. J. S.

Action of Cyanogen Bromide on Hydrazine. GUIDO PELLIZZARI and CARLO CANTONI (*Gazzetta*, 1905, **35**, i, 291—302).—The action of cyanogen chloride or bromide (1 mol.) on hydrazine (2 mols.) in aqueous solution yields:

(1) *Diaminoguanidine*, $NH{:}C(NH{\cdot}NH_2)_2$, which is unstable and could not be isolated. Its *hydrobromide*, CH_7N_5,HBr, is readily soluble in water and crystallises from alcohol in transparent, colourless plates which, in presence of the mother liquors, gradually change into small, opaque crystals melting and decomposing at 167°. The *picrate*, $CH_7N_5,C_6H_3O_7N_3$, crystallises from water in slender needles melting and decomposing at 191°, and is soluble in alcohol. The *hydrochloride* separates from alcohol in small, white crystals which gradually become opaque and melt and decompose at 185°. The *platinichloride* separates from alcohol in minute, orange-yellow crystals melting at 172—173°. All the salts of diaminoguanidine energetically reduce Fehling's solution and ammoniacal silver nitrate solution in the cold.

(2) A small quantity of p-*Di-iminohexahydrotetrazine* (*guanazine*), $NH:C<\genfrac{}{}{0pt}{}{NH\cdot NH}{NH\cdot NH}>C:NH$, which is obtained as principal product when the cyanogen bromide and hydrazine are taken in molecular proportions and is also formed by the interaction of cyanogen bromide and diaminoguanidine hydrobromide. Its *hydrobromide*, $C_2H_6N_6,HBr$, crystallises from water in a hard, white mass which melts and decomposes at 267°, and reduces Fehling's solution and ammoniacal silver nitrate solution when heated. The *picrate*, $C_2H_6N_6,C_6H_3O_7N_3$, crystallises from water in long, yellow needles melting at 276°.

In acid aqueous solution the salts of diaminoguanidine react with benzaldehyde, giving the corresponding salts of *dibenzylidenediaminoguanidine*, $NH:C(NH\cdot N:CHPh)_2$, which separates from benzene in yellow crystals melting at 180° and is readily soluble in alcohol. The *hydrobromide*, $C_{15}H_{15}N_5,HBr$, crystallises from water in a felted mass of minute needles and from alcohol in tufts of acicular crystals melting at 243°. The *hydrochloride* crystallises from water in slender needles, melts at 230°, and is readily soluble in alcohol. Both these salts assume a yellowish-red colour in the air. T. H. P.

Some Compounds of Guanidine with Sugars. ROBERT S. MORRELL and ALBERT BELLARS (*Proc. Camb. Phil. Soc.*, 1905, **13**, 79—81).—When guanidine dissolved in alcohol is added to an alcoholic solution of either dextrose, lævulose, maltose, galactose, or rhamnose, a microscopically crystalline precipitate is obtained which, in the case of the first three, is composed of three molecules of the sugar and one of guanidine, and in the case of galactose and rhamnose of molecular proportions of the two constituents; only the rhamnose compound could be crystallised. These substances, which all exhibit mutarotation, have a lower optical activity than the sugars from which they are derived. The dextrose and maltose compounds are decomposed completely by dilute hydrochloric acid. Picric acid precipitates guanidine picrate from aqueous solutions of the dextrose, lævulose, galactose, and rhamnose compounds. When heated at 100°, these compounds melt and evolve alcohol, but not ammonia; the products formed are under investigation. P. H.

***p*-Amino-acids.** THEODOR POSNER (*Ber.*, 1905, **38**, 2316—2325).—The product obtained by the action of hydroxylamine on cinnamic acid is β-hydroxylamino-β-phenylpropionic acid, and not α-hydroxylamino-β-phenylpropionic acid, as formerly supposed by the author (Abstr., 1904, i, 160). It is converted quantitatively into phenyl*iso*oxazolone identical with the product from hydroxylamine and ethyl benzoylacetate.

The compound described by Posen (Abstr., 1873, 378) as β-amino-β-phenylpropionic acid is β-phenyl-β-lactamide, and is readily obtained as leaflets melting at 120—121° by the action of ammonia on β-bromo-β-phenylpropionic acid. Cinnamamide is formed by the action of sulphuric acid on β-phenyl-β-lactamide, and not lactimide, as is erroneously supposed by Posen (*loc. cit.*).

β-Amino-β-phenylpropionic acid (*β-aminohydrocinnamic acid*),

$NH_2\cdot CHPh\cdot CH_2\cdot CO_2H$, formerly erroneously described by the author as α-aminohydrocinnamic acid, is prepared by prolonged boiling of cinnamic acid with an alcoholic solution of hydroxylamine. When heated above its melting point, it is decomposed into cinnamic acid and ammonia. The *monohydrochloride*, $C_9H_{11}O_2N,HCl$, separates from a mixture of alcohol and ether in needles and melts at 217—218°. The *trihydrochloride*, $C_9H_{11}O_2N,3HCl$, separates from concentrated hydrochloric acid in needles which soften at 228°. The *sulphate*, $(C_9H_{11}O_2N)_2,H_2SO_4$, forms glistening leaflets. The *copper*, *silver*, and *barium* salts are described. The *acetyl* derivative,

$$NHAc\cdot CHPh\cdot CH_2\cdot CO_2H,$$

melts at 161—162°.

β-Carbamidohydrocinnamic acid, $NH_2\cdot CO\cdot NH\cdot CHPh\cdot CH_2\cdot CO_2H$, prepared from the free amino-acid (or its hydrochloride) and potassium cyanate, forms hexagonal prisms and melts and decomposes at 191°. When carefully heated, it forms *phenyldihydrouracil*,

$$CHPh{<}{\genfrac{}{}{0pt}{}{CH_2\cdot CO}{NH-CO}}{>}NH,$$

which separates from alcohol in needles and melts at 216—217°.

When the solution of β-carbamidohydrocinnamic acid in concentrated sulphuric acid is warmed at 60—70° and then poured on to ice, a mixture of cinnamic acid and cyanuric acid is produced.

Phenyldihydrothiouracil, $CHPh{<}{\genfrac{}{}{0pt}{}{CH_2\cdot CO}{NH-CS}}{>}NH$, was prepared from β-amino-β-phenylpropionic acid and potassium thiocyanate.

β-Hydroxy-β-phenylpropionic acid, prepared by the action of nitrous acid on β-amino-β-phenylpropionic acid, melts at 93°. Its acetyl derivative melts at 100·5°. A. McK.

Compounds of Hydroferrocyanic and Sulphuric Acids. Sulpho-substitution in Complex Cyanides. Hydroxyferrocyanides. PAUL CHRÉTIEN (*Compt. rend.*, 1905, **141**, 37—39).—When a saturated solution of hydroferrocyanic acid in sulphuric acid is slightly diluted with water so that the precipitate first formed redissolves, the mixture after a time deposits rhomboidal tablets of the *compound* $H_4FeCy_6,7H_2SO_4$. By adding water until a permanent turbidity is produced, brilliant needles of the *substance*

$$H_4FeCy_6,5H_2SO_4$$

are obtained. Both these substances revert to hydroferrocyanic acid on exposure to damp air.

When a solution of hydroferrocyanic acid (30 grams) in 100 grams of sulphuric acid of 66° B. is heated at 100—110°, the *substance* $2H_3FeCy_6\cdot HSO_3,7H_2SO_4$ is obtained, which crystallises in colourless lamellæ. This, when placed on a porous plate and exposed to air, is converted into the *compound* $H_3FeCy_6\cdot HSO_3,H_2O$, which separates from alcohol in colourless, microscopic crystals. This is converted by barium hydroxide into barium ferrocyanide and sulphite, and, by saturation with barium carbonate in water and subsequent evaporation of the solution, into barium sulphite, ferrocyanide, and hydroxyferrocyanide.

With fuming sulphuric acid under similar conditions are obtained

needles of the *substance* $2H_2FeCy_6SO_2,3H_2S_2O_7$, which dissolves in water producing a hissing noise, and when exposed on a porous plate to moist air absorbs an atom of oxygen and is converted into a mixture of the *substance* $FeCy_6SO_2$ (slightly yellow crystals stable in moist air) with the product $H_3FeCy_6{\cdot}HSO_3$, already described. When sodium hydroxide is added to a solution of the compound $FeCy_6SO_2$ in alcohol, the *hydrated double* salt $Na_3FeCy_6(OH),Na_2SO_4,16H_2O$, crystallising in colourless needles, is obtained. Barium carbonate, under the same conditions, gives a precipitate of *barium hydroxyferrocyanide*, $Ba_2(FeCy_6{\cdot}OH)_2,4H_2O$. These products give blue colorations with ferric but not with ferrous salts. T. A. H.

Theory of Carbamide Formation. HANS EPPINGER (*Beitr. chem. Physiol. Path.*, 1905, **6**, 481—491. Compare Hofmeister, Abstr., 1897, ii, 335; Halsey, 1898, ii, 529; Schwarz, 1899, ii, 165; Plimmer, 1904, i, 538; this vol., i, 162).—When amino-acids are oxidised with permanganate in the presence of acid, hydrogen cyanide is formed, but no cyanic acid.

Glycine, when oxidised with permanganate, yields carbamide, and as an intermediate product glyoxylic acid, although neither glyoxylic acid itself nor aminoglyoxylic acid yields carbamide on oxidation in the presence of ammonia.

A distinct carbylamine odour is observed when glycine is oxidised with permanganate in the presence of aniline, and the same odour is observed when lactic, tartaric, oxalic acid, or methyl alcohol is used in place of glyoxylic acid. Small amounts of phenyl- and diphenyl-carbamide are also formed, and in the presence of methylamine small amounts of methyl- and dimethyl-carbamide. There appears to be no general parallelism between the compounds which yield carbamide on oxidation in presence of ammonia and those which yield a carbylamine odour when oxidised in presence of aniline.

A list, complete to date, is given of those substances which yield carbamide when oxidised in the presence of ammonia. J. J. S.

Action of Ammonia on Sulphuryl Chloride. BERNHARD C. STUER (*Ber.*, 1905, **38**, 2326).—Hantzsch and the author (this vol., ii, 312) stated that melanurenic acid is not formed together with carbamide, cyanuric acid, and cyamelide when dry ammonia is passed into a solution of carbonyl chloride in light petroleum at 0°. The author now finds, however, that melanurenic acid is formed under these conditions. A. McK.

Syntheses by means of Zinc Chloride. [*iso*Butyltoluene.] STANISLAS NIEMCZYCKI (*Bull. Acad. Sci. Cracow*, 1905, 2—5).—Goldschmidt's supposed *p-iso*butyltoluene (Abstr., 1882, 952), formed by heating toluene and *iso*butylalcohol with zinc chloride, yields on nitration 2 : 4 : 6-trinitro-3-*iso*butyltoluene (Bauer, Abstr., 1890, 1401; 1891, 1464), and is therefore *m-iso*butyltoluene. G. Y.

Optically Active Benzene Hydrocarbons and Phenolic Ethers. AUGUST KLAGES and RICHARD SAUTTER (*Ber.*, 1905, **38**, 2312—2315. Compare Abstr., 1904, i, 302).—d-1-iso*Propyl-3-γ-methyl-*

Δ^{α}-*pentenylbenzene*, $C_6H_4Pr\cdot CH\colon CH\cdot CHMeEt$, prepared by the action of magnesium *d*-amyl iodide on *p-iso*propylbenzaldehyde, boils at 139—140·5° under 9·5 mm. pressure, has the sp. gr. 0·8801 at 16°/4°, n_D 1·5181 and $[\alpha]_D$ +41·89° at 16°. It decolorises permanganate. Its *dibromide* is dextrorotatory, separates from aqueous alcohol in slender needles, and melts at 95—96°. When reduced by sodium and absolute alcohol, *d*-1-*iso*propyl-3-γ-methylpentenylbenzene forms d-1-iso*propyl*-3-γ-*methylamylbenzene*, $C_6H_4Pr\cdot CH_2\cdot CH_2\cdot CHMeEt$, which boils at 131—132° under 10·2 mm. pressure or at 265° under 748 mm. pressure, has the sp. gr. 0·8632 at 15·5°/4°, n_D 1·4921 and $[\alpha]_D$+15·91° at 15·5°.

d-2-*Ethoxy*-1-γ-*methyl*-Δ^{α}-*pentenylbenzene*,

$OEt\cdot C_6H_4\cdot CH\colon CH\cdot CHMeEt$,

prepared by the action of magnesium *d*-amyl iodide on *o*-ethoxybenzaldehyde, boils at 135·5—137° under 9·2 mm. pressure, has the sp. gr. 0·9406 at 15°/4°, n_D 1·5297 and $[\alpha]_D$ +40·97° at 15°. When reduced by sodium and absolute alcohol, it forms d-2-*ethoxy*-1-γ-*methylamyllenzene*, $OEt\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CHMeEt$, which boils at 126—127° under 9 mm. pressure or at 260° under 753 mm. pressure, has the sp. gr. 0·9119 at 16°/4°, n_D 1·4937 and $[\alpha]_D$ +14·99° at 16°. When converted into its sulphonic acid and then regenerated by heating the latter with water and a little hydrochloric acid for 5 hours at 160°, no racemisation has occurred.

The influence of the double linking on optical activity is exemplified in the compounds examined. A. McK.

Derivatives of *p*-Dichloro-, *p*-Dibromo-, and *v*-*m*-Dibromoiodobenzene with Polyvalent Iodine. CONRAD WILLGERODT (*J. pr. Chem.*, 1905, [ii], 71, 540—566).—[With ALBERT LANDENBERGER.]—*p*-Dichloroiodobenzene (Herschmann, Abstr., 1894, i, 330), formed by the action of potassium iodide on diazotised *p*-dichloroaniline, crystallises in large, transparent, rhombic plates which become yellow on exposure to light, melts at 21°, and distils at 255—256° under 742 mm. pressure. p-*Dichlorobenzene iodochloride*, $C_6H_3Cl_2\cdot ICl_2$, formed by the action of chlorine on *p*-dichloroiodobenzene in cooled glacial acetic acid solution, crystallises in small plates, decomposes at 108—110°, and is converted by 10 per cent. aqueous sodium hydroxide into the corresponding *iodoso*-compound, which is obtained as a yellow, amorphous powder commencing to decompose at 100°, and melting with effervescence at 193°; the *acetate*, $C_6H_3Cl_2\cdot I(OAc)_2$, forms white needles or prisms and melts and decomposes at 175°; the *basic sulphate*, $[C_6H_3Cl_2\cdot I(OH)]_2SO_4$, forms an amorphous powder melting and decomposing at 142°; after several weeks, the filtrate from the basic sulphate deposits a crystalline *substance* melting and decomposing at 150°; the *basic chromate*, $[C_6H_3Cl_2\cdot I(OH)]_2CrO_4$, forms an orange-coloured, amorphous powder, which detonates at 69—70°; the *basic nitrate*, $C_6H_3Cl_2\cdot I(OH)\cdot NO_3$, is obtained as a white powder, which melts and decomposes at 126—128°. p-*Dichloroiodoxybenzene*, $C_6H_3Cl_2\cdot IO_2$, is formed by treating the iodoso-compound with a current of steam, or by the action of aqueous

sodium hypochlorite on the iodochloride; it crystallises in microscopic, white needles and decomposes with slight detonation at 230°.

Di-p-*dichlorophenyliodonium hydroxide* is obtained as an alkaline solution which decomposes on evaporation; the chloride, $I(C_6H_3Cl_2)_2Cl$, crytallises in small prisms and melts at 176°; the *bromide* forms an amorphous, white powder and melts at 170°; the *iodide* is obtained as a yellow precipitate melting at 138°; the *nitrate* forms microscopic needles and melts at 176°; the orange-coloured, amorphous *dichromate* detonates at 148—150°; the *platinichloride* crystallises in flesh-coloured needles and melts and decomposes at 240°.

Phenyl-p-*dichlorophenyliodonium hydroxide*, $C_6H_3Cl_2\cdot IPh\cdot OH$, is obtained by treating a mixture of iodosobenzene and *p*-dichloroiodobenzene with moist silver oxide. The *chloride* crystallises in prisms and melts at 214°; the *bromide* forms white prisms and melts at 194°; the *iodide* crystallises in white prisms and melts at 132°; the *dichromate* explodes at 158°; the *platinichloride* forms microscopic, yellow needles and melts and decomposes at 198°; the *mercurichloride* forms small, colourless crystals and melts at 157°.

p-*Dichlorophenyl*-p-*tolyliodonium hydroxide*, $C_6H_3Cl_2\cdot I(C_7H_7)\cdot OH$, formed from *p*-iodosotoluene and *p*-dichloroiodobenzene, is known only in alkaline aqueous solution. The *chloride* crystallises in white needles melting at 210°; the *bromide* is obtained as a white precipitate which melts at 188°; the yellow *iodide* melts at 128°; the orange-coloured, amorphous *dichromate* detonates at 165°; the *platinichloride* crystallises in scarlet prisms and melts and decomposes at 183°.

p-*Dichlorophenyl*-p-*dichloroiodophenyliodonium hydroxide*, formed from *p*-dichloroiodosobenzene by Hartmann and Meyer's method (Abstr., 1894, i, 242), is known only in its aqueous solution, which is alkaline and almost odourless. The *chloride*, $C_6H_2Cl_2I\cdot I(C_6H_3Cl_2)Cl$, is amorphous, sinters at 125°, and melts at 156°; the *bromide* sinters at 125° and melts at 148°; the yellow *iodide* sinters at 110° and melts at 124—125°; the scarlet, amorphous *dichromate* sinters at 100° and decomposes without melting at higher temperatures; the *platinichloride* crystallises in brown prisms and melts at 198°.

p-*Dichlorophenyldichloroethyliodonium chloride*, $C_6H_3Cl_2\cdot ICl\cdot C_2H_3Cl_2$, prepared by the action of *p*-dichlorophenyl iodochloride on a compound of silver acetylide and silver chloride suspended in water (see Willgerodt and Roggatz, Abstr., 1900, i, 432), is obtained on evaporation of its aqueous solution in transparent prisms, or on addition of concentrated hydrochloric acid as a white, microcrystalline precipitate; it melts and decomposes at 178°; the *bromide* melts and decomposes at 163°; the *iodide* melts and detonates at 104°; the *dichromate* forms small, red needles, and detonates at 90—92°; the *platinichloride* forms brown needles and melts and decomposes at −147°.

[With Reinhold Thiele.]—*p*-Dibromoiodobenzene, formed from *p*-dibromoaniline, crystallises in nodular aggregates of colourless needles and melts at 38° (compare Istrati and Edeleanu, *Bull. Soc. chim.*, 1859, 1, 205). p-*Dibromobenzene iodochloride*, $C_6H_3Br_2\cdot ICl_2$, formed by chlorination of *p*-dibromoiodobenzene in glacial acetic acid chloride, forms yellow, unstable crystals, decomposes at 100° and is completely melted at 106°. When treated with 5—6 per cent.

aqueous sodium hydroxide, it yields the corresponding *iodoso*-compound, $C_6H_3Br_2 \cdot IO$, which melts and decomposes at 108°; the *acetate* crystallises in glistening, silvery leaflets and melts at 168°; the *basic nitrate* forms a white powder which detonates at 120°; the *basic sulphate* is obtained as a white powder which melts and decomposes at 122°; the *basic chromate* melts and decomposes at 43°. p-*Dibromoiodoxybenzene*, $C_6H_3Br_2 \cdot IO_2$, is formed by the action of steam on the iodoso-compound, or by the action of calcium or sodium hypochlorite on the iodochloride; it is obtained as a white, amorphous powder which explodes at 218°.

Di-p-*dibromophenyliodonium hydroxide*, $I(C_6H_3Br_2)_2 \cdot OH$, is known only in its aqueous alkaline solution; the *chloride* forms a white powder, which melts and decomposes at 185°; the *bromide* melts at 161°; the yellow, amorphous *iodide* decomposes at 101—102°; the *dichromate* is a yellow, amorphous powder which decomposes at 104—106°; the orange-coloured *platinichloride* melts and decomposes at 254°.

Phenyl-p-*dibromophenyliodonium hydroxide*, $C_6H_3Br_2 \cdot IPh \cdot OH$, forms an alkaline, aqueous solution; the white, amorphous *chloride* sinters at 150° and decomposes at 165°; the white, amorphous *bromide* melts at 177°; the *iodide*, obtained as a yellow, amorphous precipitate, melts and decomposes at 142°; the orange-coloured *dichromate* explodes at 141°; the orange-coloured *platinichloride* decomposes at 186—187°.

p-*Dibromophenyl*-p-*tolyliodonium hydroxide* forms an alkaline, aqueous solution; the white *chloride* melts at 195°; the white, amorphous *bromide* melts at 171°; the yellow, amorphous *iodide* melts and decomposes at 131°; the orange-yellow *dichromate* melts and explodes at 148°; the orange-coloured *platinichloride* melts at 191°; the *mercurichloride* forms a white, soluble powder which melts at 123°.

p-*Dibromophenyldichloroethyliodonium chloride*,

$$C_6H_3Br_2 \cdot ICl \cdot C_2H_3Cl_2,$$

is known only in solution; the white, amorphous *bromide* melts at 148°; the *iodide* melts and decomposes at 89°; the reddish-yellow, amorphous *dichromate* melts and decomposes at 86°; the orange-coloured *platinichloride* melts and decomposes at 148°.

[With PAUL FRISCHMUTH.]—v-m-*Dibromoiodobenzene*, $C_6H_3Br_2I$, formed from 2:6-dibromoaniline, crystallises in colourless, hexagonal prisms, and melts at 99°. 1:3-Dibromobenzene 2-iodochloride, $C_6H_3Br_2 \cdot ICl_2$, crystallises in small, yellow needles, melts and intumesces at 91°, and is converted by aqueous sodium hydroxide into 1:3-*dibromo-2-iodosobenzene*, $C_6H_3Br_2 \cdot IO$, which forms a brownish-yellow, amorphous powder, melts and detonates at 95°, and gradually loses oxygen, forming 1:3-dibromo-2-iodobenzene. The *acetate*, $C_6H_3Br_2 \cdot I(OAc)_2$, forms small, white crystals, melting at 170°; the *basic nitrate* is a yellow, crystalline powder which detonates slightly at 114°; the *basic iodate*, $C_6H_3Br_2 \cdot I(OH) \cdot IO_3$, forms a white powder, commences to turn brown at 160° and melts and decomposes at 240°; the *basic sulphate* is a white, amorphous powder which explodes at 150—165°; the brown, crystalline *basic chromate* decomposes at 70°.

Neither iodoxy- nor iodonium compounds could be obtained from 1 : 3-dibromo-2-iodobenzene or the corresponding iodoso-compound or its salts. G. Y.

Isomeric Dichloronitrobenzenes. F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, **7**, 668—673. Compare Abstr., 1904, i, 304).—Of the six dichloronitrobenzenes, four have been obtained in such a form that their crystallographic examination in detail has been possible. These four are (*a*) 1 : 2-dichloro-3-nitrobenzene, rhombic, [$a:b:c = 0·6472 : 1 : 0·2780$]; (*b*) 1 : 3-dichloro-2-nitrobenzene, monoclinic, [$a:b:c = 0·6696 : 1 : 0·4149$; $\beta = 87°51'$]; (*c*) 1 : 3-dichloro-5-nitrobenzene, monoclinic, [$a:b = 0·5940 : 1$; $\beta = 58°43'$]; and (*d*) 1 : 4-dichloro-2-nitrobenzene, triclinic, [$a:b:c = 0·8702 : 1 : 0·8239$; $\alpha = 92°48'$; $\beta = 112°51'$; $\gamma = 60°5'$]. The orthodichloro-derivatives are both rhombic; the metadichloro-derivatives are probably all monoclinic, and the paradichloro-derivative is triclinic. J. C. P.

Friedel and Crafts' Reaction. VII. Action of Sulphur or Sulphur Chlorides on Benzene in Presence of Aluminium Chloride. JACOB BOESEKEN (*Rec. Trav. chim.*, 1905, **24**, 209—222. Compare this vol., i, 423, 424).—Sulphur monochloride, S_2Cl_2, and sulphur dichloride, SCl_2, do not form additive compounds with aluminium chloride. When the former reacts with aluminium chloride in presence of sulphuryl chloride, Ruff's additive compound, $AlCl_3,SCl_4$, separates (Abstr., 1901, ii, 500). With benzene in presence of aluminium chloride, sulphur monochloride yields the theoretical quantity of diphenyl sulphide, required by the equation $S_2Cl_2 + 2C_6H_6 + AlCl_3 = Ph_2S,AlCl_3 + S + 2HCl$. The formation of diphenyl sulphide in this reaction is a further proof of the unsymmetrical constitution, $S\vdots SCl_2$, of sulphur monochloride (compare Lippman and Pollak, Abstr., 1901, i, 690).

When benzene is treated with sulphur dichloride in presence of aluminium chloride at 0°, diphenyl sulphide (b. p. 156° under 8 mm. and 226° under 760 mm. pressure) is almost the sole product, but at 60° there are also produced chlorobenzene and thianthrene (diphenylene disulphide), the formation of these being due to the decomposition of the sulphur chloride into the monochloride and chlorine, which then attack the benzene (compare Krafft and Lyon, Abstr., 1896, i, 297). These reactions lend support to the view that sulphur dichloride exists at low temperatures (compare Ruff and Fischer, Abstr., 1903, ii, 204, and Aten, *Thesis*, 1904).

When benzene is treated with sulphur in presence of aluminium chloride, diphenyl sulphide, thianthrene, and hydrogen sulphide are the chief products, but there is also formed a small quantity of a colourless substance, which melts at 315° and gives a green coloration when heated with aluminium chloride. Diphenyl sulphide gives a colourless additive product, $Ph_2S,AlCl_3$, with aluminium chloride, whilst the corresponding thianthrene compound, $C_{12}H_8S_2,AlCl_3$, is blue. These two substances also give respectively colourless and blue derivatives with sulphuric acid and bromine, so that possibly the latter derivatives may also be additive products. T. A. H.

Formation of Anhydrides of Sulphonic Acids by the Action of Sulphonic Chlorides on Silver Cyanate. OTTO C. BILLETER (*Ber.*, 1905, **38**, 2015—2020. Compare this vol., i, 560).—The author has previously shown that when benzenesulphonic chloride is heated at 140° with silver cyanate, a mixture of unchanged chloride and benzenesulphonecarbimide is formed (Abstr., 1904, i, 397), whilst a brown liquid solidifying to a mass of leaflets remains. The latter product has now been examined, and from it *benzenesulphonic anhydride*, $C_{12}H_{10}O_5S_2$, melting at 92° and boiling and decomposing at 240° under 10 mm. pressure, has been isolated. Its behaviour towards water and alcohol was studied quantitatively.

Benzenesulphonic anhydride is described by Abrahall (Trans., 1873, **26**, 606) as having been obtained by the action of benzenesulphonic chloride on silver benzenesulphonate; this product is, however, the free acid.

By the action of silver cyanate on methanesulphonic chloride, pure methanesulphonic anhydride was not isolated; by the action of ether on the crude product, *ethyl methanesulphonate*, $C_3H_8O_3S$, boiling at 85—86° under 10 mm. pressure, was prepared.

Methanesulphonic chloride, prepared by the action of phosphorus pentachloride on sodium methanesulphonate, boils at 161—161·5° under 730 mm. pressure and has the sp. gr. 1·48053 at 18°/4° and 1·46973 at 25°/4°. Methanesulphonic acid, prepared by the action of water on methanesulphonic chloride, boils at 167—167·5° under 10 mm. pressure and has a sp. gr. 1·4812 at 18°/4°.

Methanesulphonic anhydride, $C_2H_6O_5S_2$, prepared by heating methylsulphonic chloride with silver methylsulphonate for 3 hours at 160°, separates from ether in prisms and melts at 71°. A. McK.

Double Salts of Palladous Chloride and Bromide. ALEXANDER GUTBIER (*Ber.*, 1905, **38**, 2105—2107).—Double salts of palladous chloride and bromide with hydrochlorides or hydrobromides of organic bases are formed by adding small amounts of the latter to an excess of the palladous salt in aqueous solution. The double salts can be recrystallised from dilute hydrochloric or hydrobromic acid respectively.

Aniline palladous chloride, $(NH_3PhCl)_2,PdCl_2$, is obtained as a golden precipitate; the bromide crystallises in brown leaflets. o-*Toluidine palladous chloride*, $(NH_3C_7H_7Cl)_2,PdCl_2$, crystallises in glistening, yellowish-brown leaflets; the *bromide* forms glistening, reddish-brown needles. p-*Toluidine palladous chloride* crystallises in brown, pointed needles; the bromide forms reddish-brown needles. G. Y.

Derivatives of Palladosammine Chloride and Bromide. ALEXANDER GUTBIER (*Ber.*, 1905, **38**, 2107—2111. Compare Hardin, Abstr., 1900, ii, 85).—Derivatives of palladosammine chloride or bromide are formed by adding small amounts of palladous chloride or bromide solution to an excess of the hydrochloride or hydrobromide of an organic base dissolved in water and warming the reacting mixture.

Diphenylpalladosammine chloride, $Pd(NH_2Ph)_2Cl_2$, forms an insoluble, yellow, laminated precipitate, and, when warmed with concen-

trated ammonia, is converted into aniline and palladosammine chloride. When treated with ammonia, diphenylpalladosammine bromide yields aniline and palladosammine bromide. *Di-o-tolylpalladosammine chloride*, $Pd(C_7H_7{\cdot}NH_2)_2Cl_2$, crystallises in glistening, golden scales. *Di-o-tolylpalladosammine bromide* crystallises in small, glistening needles. *Di-p-tolylpalladosammine chloride* crystallises in glistening, golden leaflets. *Di-p-tolylpalladosammine bromide* forms small, glistening needles. When warmed with aqueous ammonia, the tolylpalladosammine chlorides and bromides yield the toluidine and palladosammine chloride or bromide respectively.

These derivatives of palladosammine chloride or bromide can be formed also by the action of an alcoholic solution of the base on palladous chloride or bromide. G. Y.

Action of Chloroacetates on Magnesium Haloid Derivatives of Aniline. F. Bodroux (*Compt. rend.*, 1905, **140**, 1597—1598. Compare Abstr., 1904, i, 662).—When magnesium phenylamine iodide, NHPh·MgI (Meunier, Abstr., 1903, i, 544), is treated with ethyl chloroacetate, there are formed iodoacetanilide, $NHPh{\cdot}CO{\cdot}CH_2I$ (m. p. 143—144°) and ethyl iodoacetate. The latter reacts feebly with magnesium phenylamine iodide, forming tarry products. With magnesium phenylamine bromide, ethyl chloroacetate yields only chloroacetanilide. When ethyl dichloroacetate or trichloroacetate reacts with magnesium phenylamine iodide, dichloroacetanilide or trichloroacetanilide are produced respectively.

Ethyl chloroacetate reacts similarly with magnesium ethiodide, forming ethyl iodoacetate (b. p. 178—180°). T. A. H.

Derivatives of Mesoxalic Esters. C. Schmitt (*Compt. rend.*, 1905, **141**, 48—49. Compare this vol., i, 508, and Curtiss, this vol., i, 507).—*Methyl mesoxalate bisanilide*, $C(NHPh)_2(CO_2Me)_2$, obtained by condensing methyl mesoxalate with aniline dissolved in acetic acid, crystallises in slender, white needles, melts at 113·5°, and is soluble in ether or alcohol, slightly so in light petroleum or toluene. It develops a blue coloration with sulphuric acid and potassium dichromate. *Ethyl mesoxalate bisanilide* melts at 103°. The corresponding *toluidine* derivative of the methyl ester begins to decompose at 120°, and melts finally at 172°. Hydrochloric acid hydrolyses these compounds into their generators, but alkalis have no action even on warming. T. A. H.

***o*-Nitrobenzyltoluidine.** F. M. Jaeger (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, **7**, 666—668).—Although this compound differs in symmetry from Nordenskiöld's para-derivative, the analogy of the two isomerides may be traced in the value of $b:c$.

o-Nitrobenzyl-*p*-toluidine : $a:b:c = 1:1:0{\cdot}623$.

o-Nitrobenzyl-*o*-toluidine : $a:b:c = 0{\cdot}8552:1:0{\cdot}6138$. J. C. P.

Action of Sulphite on Aromatic Amino- and Hydroxy-compounds. III. Preparation of Arylated β-Naphthylamines and of ββ'-Dinaphthylamines. Hans Th. Bucherer and A. Stohmann (*J. pr. Chem.*, 1905, [ii], **71**, 433—451. Compare Abstr., 1903, i, 627; 1904, i, 309, 395; this vol., i, 48).—Whilst

α-naphthol-4-sulphonic acid and resorcinol, when heated with sodium hydrogen sulphite and aniline, yield the sulphites but not the secondary amines, secondary β-naphthylamines are formed by the interaction of β-naphthyl derivatives with aromatic amines.

ββ′-Dinaphthylamine-6 : 6-disulphonic acid (D.R.-P. 114974) is formed when 1 mol. of β-naphthol-6-sulphonic acid is heated with $1\frac{1}{2}$ mols. of ammonium sulphite.

β-Naphthylamine-5-sulphonic acid differs in its behaviour from the other β-naphthyl derivatives; even in presence of 10—20 mols. of sodium hydrogen sulphite, β-naphthylamine-5-sulphonic acid forms large amounts of ββ′-dinaphthylamine-5 : 5′-disulphonic acid, which is soluble in water and, on prolonged boiling with an excess of sulphite, appears to yield traces of β-naphthol-5-sulphonic acid and ammonia. When boiled for 24 hours with sodium hydrogen sulphite and aniline in aqueous solution, β-naphthylamine-5-sulphonic acid is largely regained unchanged from the precipitate obtained on acidification.

The formation of secondary amines by this method is confined to those β-naphthols which are capable of forming sulphites. Anthraquinone derivatives do not enter into the reaction. On the other hand, the action depends on the nature of the arylamine as well as on that of the naphthyl derivative; *p*-aminophenol and *p*-phenylenediamine enter into the reaction most easily, benzidine, β-naphthylamine, and β-naphthylamine ethers least so, whilst between these extremes lie aniline, *p*-phenetidine, sulphanilic and metanilic acids, *o*- and *p*-toluidines, pararosaniline, and xylidine.

Details are given as to the proportions of β-naphthyl derivative, sodium hydrogen sulphite, arylamine, and water which give the best yields in particular cases.

It is found that, in the preparation of β-anilinonaphthalene-6-sulphonic acid with addition to the reaction mixture of a weight of dimethylaniline equal to that of the aniline, the yield is increased from 50 to 86, and with twice that weight of dimethylaniline, to 100 per cent. The results of solubility determinations of β-arylamino-naphthalenesulphonic acids in water show striking differences in the solubilities of place isomerides and other closely related compounds.

G. Y.

Derivatives of *p*-Aminotriphenylmethane. CARL THOMAE (*J. pr. Chem.*, 1905, [ii], **71**, 566—576. Compare Baeyer and Löhr, Abstr., 1890, 1141).—*Benzoyl*-p-*aminotriphenylmethane*, $C_{26}H_{21}ON$, formed by the action of benzoyl chloride on *p*-aminotriphenylmethane in alcoholic solution or in warm aqueous sodium hydroxide, crystallises in stellate aggregates of needles, melts at 198°, and is only slightly soluble in alcohol, benzene, or glacial acetic acid. When treated with fuming nitric acid in glacial acetic acid solution at 75°, it yields 3-*nitro*-4-*benzoylaminotriphenylmethane*, $C_{26}H_{20}O_3N_2$, which crystallises in small, yellow needles, melts at 138°, and is reduced by tin and hydrochloric acid to 2-phenyl-5-diphenylmethylbenziminazole. 3-*Nitro*-4-*aminotriphenylmethane*, $C_{19}H_{16}O_2N_2$, obtained by hydrolysis of the benzoyl derivative with alcoholic potassium hydroxide, crystallises

in golden leaflets, melts at 98°, is easily soluble in organic solvents, and on addition of concentrated hydrochloric acid to its alcoholic solution gives a dark red coloration, which disappears on dilution with water. 3 : 4-*Diaminotriphenylmethane*, $C_{19}H_{18}N_2$, is obtained on reduction of the nitroamino-compound with tin and hydrochloric acid as the *stannochloride*, which crystallises in yellow leaflets or stout needles; the base separates from benzene in crystals containing C_6H_6 and melting at 71—72°; the *hydrochloride* crystallises in long needles. The base gives the following characteristic reactions: with ferric chloride in aqueous solution, a reddish-brown precipitate; with sodium nitrite in cooled acid solution, a yellow precipitate which becomes white, and can be recrystallised from benzene; when fused with benzoin at 200°, a yellowish-brown *product*, which in alcoholic-ethereal solution has a green fluorescence; with chloranil in alcoholic solution a dark red coloration which is intensified by addition of concentrated hydrochloric acid; with chlorine water in alcoholic solution, a transitory red to green coloration which is more stable if produced by iodine; with bromine in carbon disulphide solution, a red precipitate. The *diacetyl* derivative, $C_{19}H_{16}N_2Ac_2$, forms large, stout crystals, melts at 226°, and is only slightly soluble in ether, benzene, or alcohol. The *dibenzoyl* derivative crystallises from a mixture of alcohol and benzene, melts at 243°, and is oxidised by chromic acid in acetic acid solution to benzamide and p-*benzoylaminodiphenylquinoylmethane*,

$$CHPh_2\cdot C\mathord{<}{\scriptstyle CO\cdot CH \atop CH\cdot CO}\mathord{>}C\cdot NHBz,$$

which crystallises in golden, glistening, short needles, melts and decomposes at about 163°, and gives a violet coloration with dilute alcoholic potassium hydroxide. p-*Benzoylaminodiphenyldihydroquinolylmethane*, $C_{26}H_{21}O_3N$, formed by reduction of the quinone with sulphur dioxide in aqueous alcoholic solution, crystallises in short, colourless needles, melts and decomposes at about 230°, and reduces boiling ammoniacal silver solution.

Anhydro-3-amino-4-benzoylaminotriphenylmethane [*2-phenyl-5-diphenylmethylbenziminazole*], $CHPh_2\cdot C_6H_3\mathord{<}{\scriptstyle NH \atop N}\mathord{>}CPh$, crystallises from benzene with C_6H_6, softens at 115—120°, and melts at 205°; the *stannochloride* crystallises in glistening leaflets or short needles; the *chromate* is yellowish-red; the *platinichloride*, $(C_{26}H_{21}N_2)_2PtCl_6$, forms rhombic plates.

3-*Nitro-4-benzoylaminotriphenylcarbinol*, $OH\cdot CPh_2\cdot C_6H_3(NO_2)\cdot NHBz$, formed by oxidation of 3-nitro-4-benzoylaminotriphenylmethane with chromic acid in boiling glacial acetic acid solution, crystallises in long, yellow needles, melts at 169°, and when warmed with alcoholic potassium hydroxide, yields a *product* which crystallises in golden leaflets, melts at 129°, and with concentrated hydrochloric acid in alcoholic solution gives a blood-red coloration which disappears on dilution with water. G. Y.

Synthesis of Three Tertiary Dimethyl*cyclo*hexanols and the Derived Hydrocarbons. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1905, **141**, 20—22).—The three dimethyl*cyclo*hexanols

were prepared by the action of magnesium methyl iodide on the three methyl*cyclo*hexanones already described (this vol., i, 275).

1 : 2-*Dimethyl*cyclo*hexanol*, prepared from 2-methyl*cyclo*hexanone, is a liquid with a camphoraceous odour, which boils at 166° (corr.), and has a sp. gr. 0·9365 at 0°/0°. When treated with zinc chloride in alcohol, it yields the corresponding *dimethyl*cyclo*hexene*, which has a disagreeable odour, boils at 132° (corr.), has a sp. gr. 0·8411 at 0°/0°, and is transformed by contact with metallic nickel at 150° (Sabatier and Senderens, Abstr., 1904, i, 156) into *dimethyl*cyclo*hexane*. The latter has a pleasant, camphoraceous odour, boils at 124° (corr.), and has a sp. gr. 0·8002 at 0°/0°.

1 : 3-*Dimethyl*cyclo*hexanol*, similarly prepared, resembles its isomeride but is slightly more viscous, boils at 169° (corr.), has a sp. gr. 0·9218 at 0°/0°, and yields a crystalline *phenylurethane* which melts at 93°. The corresponding *dimethyl*cyclo*hexene* boils at 124° and has a sp. gr. 0·8210 at 0°/0°, and on hydrogenation, by means of nickel at 150°, yields 1 : 3-*methyl*cyclo*hexane*, a colourless, mobile liquid with a slightly musty odour and a sp. gr. 0·7869 at 0°/0° and boiling at 118° (corr.). 1 : 4-*Dimethyl*cyclo*hexanol* crystallises in long, colourless needles, has a penetrating odour, melts at 50° and boils at 170° (corr.), and yields a crystalline *phenylurethane* which melts at 103°. The corresponding *dimethyl*cyclo*hexene* boils at 125° (corr.) and has a sp. gr. 0·8208 at 0°/0°. 1 : 4-*Dimethyl*cyclo*hexane* is a liquid of pleasant odour, has a sp. gr. 0·7861 at 0°/0°, and boils at 119° (corr.). T. A. H.

Aromatic Nitrocarbonic Esters and their Reduction Products. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and F. PERRIN (*Bull. Soc. chim.*, 1905, [iii], **33**, 710—712).—*Nitrophenyl ethyl carbonate* $NO_2·C_6H_4·O·CO_2Et$, prepared by treating phenyl ethyl carbonate, dissolved in acetic acid, with fuming nitric acid, separates from alcohol in pale yellow crystals, and melts at 65—66°. On reduction with stannous chloride, it yields the corresponding *amino*-compound, which is a yellow, syrupy liquid. The *acetyl* derivative of the amine melts at 118—119°, and the corresponding *carbamide*,

$$NH_2·CO·NH·C_6H_4·O·CO_2Et,$$

melts at 151—152°.

o-*Nitromethoxyphenyl ethyl carbonate*, similarly prepared, forms yellow crystals and melts at 98—99°; the corresponding *amino*-compound separates in slightly yellow crystals, melts at 69—70°, and yields an *acetyl* derivative melting at 118°. The *carbamide*,

$$NH_2·CO·NH·C_6H_3(OMe)·O·CO_2Et,$$

melts at 161—162°. T. A. H.

Action of Chloro-formodiethylamide on Nitrophenols and Reduction of the Corresponding Derivatives. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and F. PERRIN (*Bull. Soc. chim.*, 1905, [iii], **33**, 712—713. Compare Abstr., 1904, i, 559).—When *p*-nitrophenol is warmed with chloro-formodiethylamide, a syrupy *nitro*-derivative is formed, and this on reduction with stannous chloride in presence of hydrochloric acid yields the corresponding p-*nitrophenyl diethylcarbamate*, $NH_2·C_6H_4·O·CO·NEt_2$, which forms large, yellow crystals

and melts at 62°. The *acetyl* derivative melts at 90—91° and the *carbamide* at 159—160°.

Nitro-o-methoxyphenyl diethylcarbamate, similarly prepared from nitroguaiacol, is crystalline and melts at 83°. The corresponding *amino*-compound is a syrup, but yields a crystalline *acetyl* derivative melting at 122—123° and a *carbamide* which melts at 170—171°.

T. A. H.

Grignard's Reaction with Dihaloids. Carl A. Bischoff (*Ber.*, 1905, **38**, 2078—2083. Compare Grignard and Tissier, Abstr., 1901, i, 316; Ahrens and Stapler, this vol., i, 423).—The interaction of magnesium and ethylene dibromide in ethereal solution is not affected by the presence of a molecular proportion of anisole, but is retarded by addition of a molecular proportion of phenetole, ethyl acetate, or benzil, or by dilution with an excess of ether (from 10 to 70 c.c.) or with benzene. With ethyl acetate, the retardation is the greater the more nearly pure the ester. No reaction takes place even on boiling or on addition of traces of iodine or alcohol, in presence of molecular proportions of acetone, acetophenone, benzophenone, or ethyl oxalate, malonate, or succinate. The reaction takes place slowly in presence of traces of these substances.

The action of the additive compounds formed from 1 mol. of ethylene dibromide, or from 1 mol. of trimethylene dibromide and 1 mol. of magnesium in ethereal solution on 1 mol. of benzil, leads to partial reduction of the benzil to benzoin. On addition of 1 mol. of benzil to the additive compound from 2 mols. of ethylene dibromide with 1 mol. of magnesium, no benzoin is formed, but a *product*, which crystallises in colourless needles and melts at 85°, is obtained.

The action of quinone on the additive compound of ethylene dibromide and magnesium leads to the formation of a green to black mass which is oxidised on exposure to air.

Ethyl succinate does not enter into reaction with magnesium ethylene dibromide.

G. Y.

2-β-Aminoethylphenol and its Methyl Ether. Robert Pschorr and Hans Einbeck (*Ber.*, 1905, i, 2067—2077. Compare Pschorr and Massacin, Abstr., 1904, i, 767).—Contrary to Zwenger's statement (*Annalen*, 1863, **126**, 262), ethyl melilotate cannot be purified by distillation, as it is partially converted into hydrocoumarin.

Melilotylhydrazide, $C_9H_{12}O_2N_2$, formed by the action of hydrazine hydrate in 50 per cent. solution on hydrocoumarin, crystallises from water in colourless leaflets or aggregates of needles, melts at 164—165°, and reduces Fehling's solution when slightly warmed. The *hydrochloride*, $C_9H_{12}O_2N_2,HCl$, formed along with a small quantity of *s*-dimelilotylhydrazide, by the action of concentrated hydrochloric acid on the hydrazide, crystallises in stellate aggregates of rhombic leaflets and melts at 157—158°.

s-*Dimelilotylhydrazide*, $C_{18}H_{20}O_4N_2$, which is formed by warming melilotylhydrazide with dilute acetic acid, or with evolution of gas, by treating it with sodium nitrite in cold dilute acetic acid solution, crystallises in glistening scales and melts at 176—177°.

The action of sodium nitrite on melilotylhydrazide hydrochloride in aqueous solution under a layer of ether, leads to the formation of the *azoimide*; after evaporation of the ethereal solution, and boiling the residue with alcohol, the impure azoimide is obtained as an oil, which partly solidifies in a vacuum, and when distilled under 30—40 mm. pressure yields hydrocoumarin and s-*di*-o-*hydroxy-β-phenylethylcarbamide*, $CO(NH\cdot CH_2\cdot CH_2\cdot C_6H_4\cdot OH)_2$; this crystallises in long leaflets, melts at 187—188°, and distils at 250—280° under 15 mm. pressure. When heated with alcoholic hydrochloric acid in a sealed tube at 150—160° for 4 hours, the carbamide is hydrolysed to 2-*β-aminoethylphenol* (o-*hydroxy-β-phenylethylamine*), which is obtained as the *hydrochloride*, $OH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot NH_2,HCl$, crystalling in stellate aggregates of rhombic leaflets and melting at 152—153°.

o-*Hydroxy-β-phenylethyltrimethylammonium iodide*, $C_{11}H_{18}ONI$, formed by warming the hydrochloride with sodium and methyl iodide in alcoholic solution, crystallises in prisms, melts at 217—218°, and when distilled with concentrated aqueous sodium hydroxide yields trimethylamine and hydrocoumarone.

Methyl o-*methoxyphenylpropionate*, $OMe\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CO_2Me$, formed by the action of methyl sulphate on melilotic acid in aqueous sodium hydroxide solution, is a colourless, highly refractive oil, which boils at 274—275° under 768 mm. pressure, and when boiled with hydrazine hydrate forms the *hydrazide*, $OMe\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CO\cdot N_2H_3$; this crystallises in glistening, colourless, delicate needles and melts at 83—84°. The action of sodium nitrite on the hydrazide in dilute acetic acid solution leads to the formation of s-*di*-o-*methoxyphenylpropionylhydrazide*, $C_{20}H_{24}O_4N_2$, which crystallises in long needles, melts at 185—186°, and when heated with methyl alcoholic hydrochloric acid is hydrolysed to hydrazine and methyl *o*-methoxyphenylpropionate. The *hydrochloride* of *o*-methoxyphenylpropionylhydrazide, $C_{10}H_{14}O_2N_2,HCl$, crystallises in slender, colourless needles, melts at 166—167°, and when treated with sodium nitrite in aqueous solution under ether yields the azoimide, which when boiled with absolute alcohol forms *ethyl* o-*methoxyphenylcarbamate*, $OMe\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot NH\cdot CO_2Et$. This is a viscid, colourless oil, which boils at 200° under 19 mm. pressure, and when heated with concentrated aqueous ammonia in a sealed tube at 180° for 5 hours is hydrolysed to o-*methoxy-β-phenylethylamine*, $OMe\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot NH_2$. This base is an oil which boils at 236—237°, is easily soluble in ether, and absorbs carbon dioxide from the air. The *hydrochloride*, $C_9H_{13}ON,HCl$, crystallises in long, prismatic plates and melts at 141°; the quaternary *methiodide*, $C_9H_{11}ONMe_3I$, crystallises in needles and melts at 209°. *o*-Methoxystyrene, $C_9H_{10}O$, formed by heating the quaternary iodide with sodium ethoxide in alcoholic solution at 100° under pressure, is a colourless, mobile liquid, which has a characteristic, intense odour, and boils at 82—83° under 18 mm. pressure (Perkin, Trans., 1881, **39**, 411).

o-Methoxybenzaldehyde and magnesium methyl iodide react to form o-*methoxyphenylmethylcarbinol*, $C_9H_{12}O_2$, which is an oil with a pleasant odour, boiling at 124—126° under 17 mm. pressure. When distilled under the atmospheric pressure or when treated with dehydrating

agents, the carbinol forms waxy products which are probably polymerides of *o*-methoxystyrene. G. Y.

Aromatic Monosubstituted Ethylene Oxides. Ernest Fourneau and Marc Tiffeneau (*Compt. rend.*, 1905, **140**, 1595—1597. Compare this vol., i, 523).—These substances are prepared by submitting the monosubstituted ethylenes suspended in wet ether to the action of iodine and yellow mercuric oxide. The yield in the following cases varies from 50 to 100 per cent. of the theoretical.

Styrene oxide, $CHPh{<}\overset{CH_2}{\underset{O}{|}}$.—This is an aromatic liquid which boils at 84—88° under 14—15 mm. and at 188—192° under atmospheric pressure, has a sp. gr. 1·067 at 0° and 1·045 at 24°. When heated with metallic catalytic agents at 200°, it is converted into the isomeric phenylacetaldehyde. Sodium hydrogen sulphite, sulphurous acid, silver nitrate, and mercuric oxide have no action on styrene oxide, and it is also unaffected by boiling dilute sulphuric acid. *Allylbenzene oxide*, $CH_2Ph\cdot CH{<}\overset{CH_2}{\underset{O}{|}}$, boils at 94—98° under 15 mm. pressure. *Estragole oxide*, $OMe\cdot C_6H_4\cdot CH_2\cdot CH{<}\overset{CH_2}{\underset{O}{|}}$, boils at 153—156° under 20 mm. pressure, and has a sp. gr. 1·149 at 0°.

Phenylpropylene oxide, $\begin{matrix}CHPh\\ | \\ CHMe\end{matrix}{>}O$, has a sp. gr. 1·028 at 0°, boils at 90—95° under 15 mm. pressure, and is at the same time partially converted into the isomeric aldehyde. T. A. H.

Condensation of Catechol with Ketones. Rudolf Fabinyi and Tibor Széky (*Ber.*, 1905, **38**, 2307—2312).—The *compound* $C_{21}H_{24}O_4$, prepared by the condensation of catechol with acetone by heating with glacial acetic acid and hydrochloric acid of sp. gr. 1·19 in a sealed tube at 145°, crystallises from alcohol in needles and melts and decomposes at 314—316°. The action is represented by the equation $2C_6H_4(OH)_2 + 3COMe_2 = C_{21}H_{24}O_4 + 3H_2O$. Its *tetracetyl* derivative forms white crystals and melts at 174°; its *tetrabenzoyl* derivative separates from glacial acetic acid in glistening leaflets and melts at 234°. Its *tetrabromo*-derivative, $C_{21}H_{20}O_4Br_4$, crystallises in needles and melts and decomposes at 130°. Its *tetrabromotetracetyl* derivative crystallises in tiny leaflets and melts and decomposes at 240°.

When oxidised by nitric acid, the condensation product in question yields the *compound* $C_{21}H_{20}O_4$, which forms dark red crystals. The tetra-acetyl and tetrabenzoyl derivatives cannot be oxidised in a similar manner, from which it is concluded that the elimination of the four hydrogen atoms takes place from the hydroxyl groups. The tetrabromo-derivative is oxidised to form the *compound* $C_{21}H_{18}O_4Br_4$, which separates from nitrobenzene in glistening needles.

The *compound* $C_{24}H_{30}O_4$, prepared by the condensation of catechol with methyl ethyl ketone, separates from glacial acetic acid in

leaflets and melts at 302—305°. Its *tetracetyl* derivative melts at 165—166°.

The *compound* $C_{27}H_{36}O_4$, prepared by the condensation of catechol with diethyl ketone, is formed in small yield.

Tentative formulæ are adduced for the condensation products described. A. McK.

Eugenol and Certain of its Derivatives. GEORGE B. FRANKFORTER and MAX LANDO (*J. Amer. Chem. Soc.*, 1905, **27**, 641—649. Compare Chasanowitz and Hell, Abstr., 1885, 779).—The purified eugenol used in these experiments had the following physical properties; boiling point, 244·5°; sp. gr., 1·0689 at 20°; n_D, 1·54437; molecular heat of combustion, 1304 cal.; specific heat, 0·5024. The *lithium* and *lead* derivatives of eugenol are described.

By the addition of bromine to a solution of eugenol in chloroform cooled to below 0°, a dark, amorphous mass is obtained. On distilling this product with steam, a residue is obtained consisting of *bromoeugenol bromide*, $OMe\cdot C_6H_2Br(OH)\cdot CH_2\cdot CHBrMe$, which forms a nearly white, granular mass; this substance is converted by potassium hydroxide into *bromoeugenol hydroxide*, $C_{10}H_{13}O_3Br$, which forms a white, amorphous powder and melts at 79—82°.

Tribromoeugenol bromide, $C_{10}H_{10}O_2Br_4$, separates from alcohol in large, nearly colourless, triclinic crystals, melts at 118·5°, is soluble in ether, insoluble in water, and is not identical with the tetrabromo-compound described by Chasanowitz and Hell (*loc. cit.*). When this substance is warmed with dilute potassium hydroxide, *tribromoeugenol hydroxide*, $C_{10}H_{11}O_3Br_3$, is obtained as a white, amorphous precipitate which is soluble in chloroform and melts at 137°.

When chlorine is led into a solution of eugenol in chloroform, cooled by means of a freezing mixture, a *pentachloro*-compound, $C_{10}H_9O_2Cl_5$, is obtained as a red, crystalline substance; by the action of zinc dust on a solution of this substance in 90 per cent. alcohol, a *zinc* compound, $C_{20}H_{16}O_4Cl_6Zn$, is produced as a white powder. If the pentachloro-compound is treated with potassium hydroxide, *trichloroeugenol hydroxide*, $C_{10}H_{11}O_4Cl_3$, is obtained as an amorphous, brown powder.

When sulphur dichloride is added to an ethereal solution of eugenol, *thiodieugenol dichloride*, $C_{20}H_{24}O_4SCl_2$, is produced as a bright red precipitate. E. G.

Oxides of Propenylphenol Ethers and their Conversion into the Isomeric Ketones. PAUL HÖRING (*Ber.*, 1905, **38**, 2296—2299. Compare Pond and Siegfried, Abstr., 1903, i, 417).—The action of nitric acid on *iso*safrole dibromide in glacial acetic acid solution leads to the formation of *nitro*-3 : 4-*methylenedioxy*-1-β-*bromo*-α-*acetoxy*-n-*propylbenzene*, $CH_2{:}O_2{:}C_6H_2(NO_2)\cdot CH(OAc)\cdot CHBrMe$, which melts at 113°, and is converted by alcoholic potassium hydroxide into *nitroisosafrole oxide*, $CH_2{:}O_2{:}C_6H_2(NO_2)\cdot CH\Big<\begin{matrix}CHMe\\ \vert \\ O\end{matrix}$, melting at 113—114°.

In the same manner, when treated with alcoholic potassium hydroxide, the α-acetoxy-β-bromo-derivatives which are formed by the action of sodium acetate on the dibromides of anethole, *iso*safrole, and their

bromo-derivatives, are converted into the corresponding oxides: *anethole oxide*, $OMe\cdot C_6H_4\cdot CH<\overset{CHMe}{\underset{O}{|}}$, boils at 132° under 11 mm. pressure; iso*safrole oxide*, $CH_2{:}O_2{:}C_6H_3\cdot CH<\overset{CHMe}{\underset{O}{|}}$, boils at 140—142° under 9 mm. pressure; *bromo*iso*safrole oxide*,

$$CH_2{:}O_2{:}C_6H_2Br\cdot CH<\overset{CHMe}{\underset{O}{|}},$$

boils at 169—173° under 11 mm. pressure; *dibromo*iso*safrole oxide*, melts at 134—135°. These oxides, which are obtained also by the action of alcoholic potassium hydroxide on the β-bromo-α-hydroxy-derivatives which are formed on treating the corresponding dibromides with aqueous acetone, undergo isomeric change into the β-ketones when distilled under the ordinary pressure or when warmed with dilute acids.

Anethole ketone, $OMe\cdot C_6H_4\cdot CH_2\cdot COMe$, boils at 262—264°; *iso*-safrole ketone, $CH_2{:}O_2{:}C_6H_3\cdot CH_2\cdot COMe$, boils at 283—284° (compare Wallach, Abstr., 1904, i, 753); *bromo*iso*safrole ketone*,

$$CH_2{:}O_2{:}C_6H_2Br\cdot CH_2\cdot COMe,$$

melts at 103°; *dibromo*iso*safrole ketone*, $CH_2{:}O_2{:}C_6HBr_2\cdot CH_2\cdot COMe$, melts at 116—117°. G. Y.

Reduction of Aromatic Amino-acids to the Corresponding Alcohols. St. Langguth (*Ber.*, 1905, **38**, 2062—2064. Compare Herrmann, *Annalen*, 1864, **132**, 75; Mettler, this vol., i, 436).—*m*-Aminobenzoic acid is reduced by 4 per cent. sodium amalgam in hot hydrochloric acid solution to *m*-aminobenzyl alcohol, which melts at 97°, and can be distilled without decomposition in a vacuum. When diazotised and coupled with β-naphthol in alkaline solution, *m*-aminobenzyl-alcohol forms m-*hydroxymethylbenzene-azo-β-naphthol*, $C_{17}H_{14}O_2N_2$, which crystallises in purple-red needles and melts at 127°.

m-*Iodobenzyl alcohol*, which is formed by the action of potassium iodide and powdered copper on diazotised *m*-aminobenzyl alcohol, is a colourless oil which boils at 154° under 10 mm. pressure.

The action of cuprous cyanide on *m*-aminobenzyl alcohol leads to the formation of m-*methylolbenzonitrile* [ω-*hydroxy*-m-*toluonitrile*], $OH\cdot CH_2\cdot C_6H_4\cdot CN$, which is a colourless oil; it boils at 165° under 16 mm. pressure, and is converted by aqueous potassium hydroxide into m-*methylolbenzoic* [ω-*hydroxy*-m-*toluic*] *acid*, $OH\cdot CH_2\cdot C_6H_4\cdot CO_2H$. This forms a white, crystalline powder, melts at 111°, and boils at 190° under 11 mm. pressure.

o-Aminobenzyl alcohol may be prepared by the reduction of anthranilic acid with sodium amalgam in hydrochloric acid solution, but only small quantities of *p*-aminobenzyl alcohol are obtained by the reduction of *p*-aminobenzoic acid. G. Y.

Synthesis of Monohydric and Polyhydric Alcohols. Victor Grignard (*Compt. rend.*, 1905, **141**, 44—46).—The method consists in treating the haloid derivatives of alcohols with mixed organo-

magnesium compounds; thus in the case of glycol chlorohydrin the reaction represented by the following equation takes place,

$$RMgX + CH_2Cl\cdot CH_2\cdot OH = RH + CH_2Cl\cdot CH_2\cdot OMgX.$$

The complex so formed is capable of reacting with a further quantity of the same or a new organo-magnesium compound thus,

$$R'MgX' + CH_2Cl\cdot CH_2\cdot OMgX = MgX'Cl + R'CH_2\cdot CH_2\cdot OMgX.$$

The first reaction takes place in the cold and the second while the ether used as solvent is being distilled off. The addition of water to the residue liberates the desired alcohol. From glycol chlorohydrin, phenylethyl alcohol and the following alcohols were prepared by the use of appropriate aromatic organo-magnesium compounds. The yield in each case was about 80 per cent. o-*Tolylethyl alcohol* is an aromatic liquid, boils at 119—120° under 14 mm. and at 237—239° (corr.) under 740 mm. pressure, has a sp. gr. 1·020 at 0° and 1·0095 at 14·8°/4° and n_D 1·53472: the *phenylurethane* melts at 67°. p-*Tolylethyl alcohol* boils at 115—116° under 13 mm. pressure, has a sp. gr. 1·0119 at 0°, 1·0028 at 13°/4°, and n_D 1·52985: the *phenylurethane* melts at 112°. p-*Methoxyphenylethyl alcohol* has an anise-like odour, melts at 24°, boils at 143—144° under 13 mm. pressure, and gives a *phenylurethane* which melts at 123—124°. α-*Naphthylethyl alcohol* melts at 62° and boils at 186° under 17 mm. pressure; the *phenylurethane* melts at 115°.

With glycerol α-monochlorohydrin, magnesium phenyl bromide furnishes a viscous *glycol* which sets to a glassy solid at −60°, boils at 163—165° under 12 mm. pressure, and gives an *acetyl* derivative, which boils at 159—161° under 12 mm. pressure. On oxidation with chromic acid, it yields acetophenone, benzoic acid, and phenylacetic acid, and on distillation at the ordinary temperature undergoes partial dehydration, forming hydratropic acid. This product is probably a mixture of the expected glycol, $CH_2Ph\cdot CH(OH)\cdot CH_2\cdot OH$, and Tiffeneau's glycol, $OH\cdot CMePh\cdot CH_2\cdot OH$.

Similarly, when glycerol α-monochlorohydrin is treated with magnesium *iso*amyl bromide a viscous *glycol*, which boils at 128—133° under 12 mm. pressure and seems to have the constitution

$$CHMe_2\cdot CH_2\cdot CH_2\cdot CMe(OH)\cdot CH_2\cdot OH,$$

is the principal product. It is probable that in this case the complex first formed is $\begin{matrix} CH_2 \\ | \\ O \end{matrix}\!\!>\!CH\cdot CH_2\cdot OMgBr$, and that this becomes transformed into the ketone, $CH_3\cdot CO\cdot CH_2\cdot OMgBr$, which then reacts normally (Abstr., 1903, i, 552). T. A. H.

A Dihydric Alcohol Related to Phytosterol. TIMOTHÉE KLOBB (*Compt. rend.*, 1905, **140**, 1700—1701).—The crystalline substance arnisterol, obtained from *Arnica montana* (Abstr., 1904, i, 410), yields derivatives which indicate that it contains two alcoholic hydroxyl groups. When heated with acetic anhydride at 140—150°, a diacetyl derivative, $C_{28}H_{44}(OAc)_2$, is formed. This is usually obtained in the form of large octahedra (α-acetate) which melt at 181—183°; but sometimes long prisms (β-acetate) are obtained which melt at 100—101° and occasionally an amorphous acetate makes its appearance. In benzene solution (4 grams per 100 c.c.), the α-acetate has a

rotation $[\alpha]_D$ +74·2°, and a molecular weight according to cryoscopic measurements equal to 485 (calculated 498).

A dibenzoyl derivative, $C_{28}H_{44}(OBz)_2$, is obtained from arnisterol by treatment with benzoyl chloride. It melts at 223° and is almost insoluble in cold alcohol. Its molecular weight in benzene solution was found to be equal to 586 (calculated 622).

A phenylurethane, $C_{28}H_{44}(O{\cdot}CO{\cdot}NHPh)_2$, is obtained when arnisterol is treated with phenylcarbimide in benzene solution. It can be readily crystallised from boiling ether, and melts and decomposes at about 200°. The molecular weight in acetic acid and ethylene bromide solutions when extrapolated to zero concentration was found to be equal to 624 and 595 respectively (calculated 652). It appears probable that arnisterol is a dihydric alcohol and the name *arnidiol* is proposed for it. H. M. D.

Action of Potassium Cyanide on Potassium *m*-Nitrobenzenesulphonate. M. Holleman (*Rec. trav. chim.*, 1905, **24**, 194—208).—When potassium *m*-nitrobenzenesulphonate is heated in closed tubes at 180—200° with an aqueous solution of potassium cyanide, the following products are formed: potassium *p*-sulphobenzoate, potassium *o*-sulphobenzoate, 2-amino-4-sulphobenzoic acid, 6-amino-2-sulphobenzoic acid, and 4-amino-2-sulphobenzoic acid. When the reaction is allowed to proceed at 100°, resinous products and amines are produced in addition to the potassium salts of *o*- and *p*-sulphobenzoic acids. No azoxy-compounds or hydrazine derivatives are formed in either case. Lobry de Bruyn's explanation of the results obtained by Richter in treating *m*-chloronitrobenzene with potassium cyanide is applicable to these cases (Abstr., 1904, i, 388).

2-*Amino*-4-*sulphobenzoic acid* decomposes without melting when gently heated on platinum foil and dissolves in water, giving a blue, fluorescent solution. When diazotised and combined with dimethylaniline, it yields a dye resembling helianthin in colour. 6-*Amino*-2-*sulphobenzoic acid* crystallises in agglomerations of slender needles and exhibits reactions similar to those of the foregoing isomeride. 4-*Amino*-2-*sulphobenzoic acid* crystallises in fine needles and gives the same reactions as the two foregoing isomerides, but its solution in water is not fluorescent.

The *diamide* of *p*-sulphobenzoic acid, $NH_2{\cdot}SO_2{\cdot}C_6H_4{\cdot}CO{\cdot}NH_2$, melts at 230°. The *sulphoimide* of *o*-sulphobenzoic acid, obtained by the action of phosphorus pentachloride and ammonium carbonate on the acid, melts at 220°.

When 3-nitro-*p*-toluenesulphonic acid or *m*-nitrobenzenesulphonamide is heated with an aqueous solution of potassium cyanide only resinous products are formed. 3-Nitro-*p*-toluenesulphonamide melts at 142·5° (Otto and Gruber give 128° as the melting point).

T. A. H.

Action of Thionyl Chloride on Thiobenzamide. Leon Tochtermann (*Bull. Acad. Sci. Cracow*, 1905, 1—2. Compare Michaelis, Abstr., 1893, i, 504, 515).—The action of thionyl chloride

on benzamide leads to the formation of three products, which are separated by fractional crystallisation from benzene.

(1.) *Benzoylthiobenzamide*, NHBz·CSPh, is a red substance which melts at 117°, is soluble in organic solvents, reacts with phenylhydrazine, and when treated with silver oxide yields dibenzamide.

(2.) A *substance* which crystallises in long, white needles, melts at 88—90°, is indifferent, and may have the constitution

$$CH_2Ph\cdot N<\begin{matrix}N\cdot CPhS\\ | \\ N\cdot CPhS\end{matrix}.$$

The third product, which was formed in small quantity, could not be purified. G. Y.

Preparation of the Decomposition Products (containing Halogens) from Piperidine. JULIUS VON BRAUN and ADOLPH STEINDORFF (*Ber.*, 1905, **38**, 2336—2339. Compare Abstr., 1904, i, 841, 918, 970, 1019; this vol., i, 206, 341).—An improved method for the preparation of benzoyl-ε-chloroamylamide, $NHBz\cdot[CH_2]_4\cdot CH_2Cl$, from benzoylpiperidine and phosphorus pentachloride, is described. The *compound*, $2NHBz\cdot[CH_2]_4\cdot CH_2Cl,CaCl_2$, formed by allowing fused calcium chloride to remain in contact with an ethereal solution of benzoyl-ε-chloroamylamide for some time, forms a white powder which is stable in the air and melts at 148—149°.

A mixture of benzonitrile and αε-dibromopentane is formed when benzoylpiperidine is distilled with phosphorus bromide. A method is described by which the benzonitrile may readily be separated from the mixture. A. McK.

Chloromethoxybenzoic Acid. FRITZ ULLMANN and HERMANN KIPPER (*Ber.*, 1905, **38**, 2120—2126. Compare preceding abstract; Ullmann, Abstr., 1903, i, 692; Ullmann and Schlaepfer, Abstr., 1904, i, 570; Goldberg, this vol., i, 59; Ullmann and Lebner, *ibid.*, i, 289).—When heated with piperidine, water, and copper powder under pressure at 160° for 4 hours, or with dimethylamine, water, and copper powder at 135°—140° for 5—6 hours, 6-chloro-3-methoxybenzoic acid yields 5-methoxysalicylic acid. Under similar conditions, *o*-chlorobenzoic acid yields salicylic acid.

2-*Phenoxy*-5-*methoxybenzoic acid*, $OMe\cdot C_6H_3(OPh)\cdot CO_2H$, is formed by the condensation of phenol and 6-chloro-3-methoxybenzoic acid by means of sodium methoxide and copper. It crystallises in colourless leaflets, melts at 156°, and when warmed with concentrated sulphuric acid yields 2-methoxyxanthone. When warmed with aluminium chloride in xylene solution, this yields methyl chloride and 2-hydroxyxanthone, which crystallises in matted, yellow needles, and melts at 240° (m. p. 231°; Kostanecki and Rutishauser, Abstr., 1892, 1096).

2-β-*Naphthoxy*-5-*methoxybenzoic acid*, $C_{18}H_{14}O_4$, crystallises in stellate aggregates of colourless needles, melts at 160°, dissolves in concentrated sulphuric acid to a colourless solution, which when warmed becomes brown with green fluorescence, and when treated

with phosphorus pentachloride and aluminium chloride in benzene solution yields 2-*methoxynaphthaxanthone*,

$$CH{<}\begin{matrix}C_6H_4\cdot C{-}O{-}C\cdot CH{:}CH \\ CH{-}C\cdot CO\cdot C\cdot CH{:}C\cdot OMe\end{matrix},$$

which crystallises in colourless needles, and melts at 256°. With a slightly larger proportion of aluminium chloride and a longer period of heating, the product is 2-hydroxynaphthaxanthone, $C_{17}H_{10}O_3$, which crystallises in brown needles, melts at 287—290°, and dissolves in dilute sodium hydroxide to a yellow solution, or in concentrated sulphuric acid to a yellow solution with green fluorescence. The *sodium* derivative crystallises in yellow needles.

6-*Anilino-3-methoxybenzoic acid*, $NHPh\cdot C_6H_3(OMe)\cdot CO_2H$, is obtained by heating aniline and 6-chloro-3-methoxybenzoic acid with a small amount of copper powder, or by boiling aniline, potassium 6-chloro-3-methoxybenzoate, potassium carbonate, and copper powder in amyl alcohol solution in a reflux apparatus. It crystallises in yellow needles, melts at 158°, is readily soluble in alcohol or glacial acetic acid to yellow, or in aqueous alkali hydroxides to colourless solutions, and when heated on the water-bath with concentrated sulphuric acid yields 3-*methoxyacridone*, $C_6H_4{<}\begin{matrix}NH\cdot C{:}CH\cdot CH \\ CO{-}C{:}CH\cdot C\cdot OMe\end{matrix}$. This crystallises in yellow needles, melts at 282—284°, and dissolves in concentrated sulphuric acid, alcohol, or glacial acetic acid to solutions with green, or in benzene or toluene to solutions with blue fluorescence.

6-o-*Methoxyanilino-3-methoxybenzoic acid*,

$$OMe\cdot C_6H_4\cdot NH\cdot C_6H_3(OMe)\cdot CO_2H,$$

formed from *o*-anisidine and 6-chloro-3-methoxybenzoic acid, crystallises in glistening, yellow, prismatic needles, melts at 192°, and dissolves in concentrated sulphuric acid to an emerald green solution, which, on warming, becomes brown with green fluorescence.

6-*β-Naphthylamino-3-methoxybenzoic acid*,

$$C_{10}H_7\cdot NH\cdot C_6H_3(OMe)\cdot CO_2H,$$

formed from *β*-naphthylamine and 6-chloro-3-methoxybenzoic acid, crystallises in yellow needles and melts at 171°. G. Y.

Arylsalicylic [Aryloxybenzoic] Acids and their Conversion into Xanthones. FRITZ ULLMANN and MARGUERITE ZLOKASOFF (*Ber.*, 1905, **38**, 2111—2119. Compare Abstr., 1904, i, 417).—Aryloxybenzoic acids are formed by the condensation of potassium *o*-chlorobenzoate with the potassium derivative of the phenol in presence of copper powder. The aryloxybenzoic acids are mostly converted into the corresponding xanthones by the action of concentrated sulphuric acid.

o-*Tolyloxybenzoic acid*, $C_7H_7\cdot O\cdot C_6H_4\cdot CO_2H$, crystallises in colourless needles, melts at 133·5°, and is easily soluble in alcohol, ether, or benzene. 4-Methylxanthone, $C_6H_4{<}\begin{matrix}O{-}C{:}CMe\cdot CH \\ CO\cdot C{:}CH{-}CH\end{matrix}$, crystallises in white needles, melts at 126° (m. p. 105°; Schoepff, Abstr., 1893, 217), and dissolves in concentrated sulphuric acid to a yellow solution with green fluorescence.

m-*Tolyloxybenzoic acid* crystallises in needles, melts at 95°, and forms 1-(or 3-)methylxanthone, which crystallises in large, stellate aggregates of leaflets, and melts at 89—91°. Weber's 3-methylxanthone (Abstr., 1892, 1092; compare Strobach, Abstr., 1902, i, 171) was probably 3 : 5-dimethylxanthone.

p-*Tolyloxybenzoic acid* forms large crystals, melts at 118·5°, and yields 2-methylxanthone, which crystallises in large needles, melts at 121° (m. p. 105°; Graebe and Feer, Abstr., 1887, 152), and dissolves in concentrated sulphuric acid to a yellow solution with green fluorescence.

1 : 3 : 4-*Xylyloxybenzoic acid* crystallises in almost colourless needles, melts at 152°, dissolves readily in alcohol, ether, or boiling benzene, and forms 2 : 4-*dimethylxanthone*, $C_{15}H_{12}O_2$, which crystallises in large, glistening, transparent leaflets, melts at 152°, and dissolves in concentrated sulphuric acid to an intensely yellow solution, with green fluorescence.

β-Naphthyloxybenzoic acid crystallises in white needles, melts at 124°, and dissolves in concentrated sulphuric acid to a colourless solution, which when warmed becomes brownish-yellow with a green fluorescence, the β-naphthoxy-acid forming β-phenonaphthaxanthone in a 20 per cent. yield, the remainder being apparently sulphonated. Better yields of β-phenonaphthaxanthone (Kostanecki, Abstr., 1892, 1099) are obtained by heating the β-naphthoxy-acid in benzene solution with phosphorus pentachloride and with aluminium chloride successively.

Salicylic acid o-*methoxyphenyl ether* forms small, almost colourless, glistening crystals, melts at 112°, and, when heated in benzene solution with phosphorus pentachloride and with aluminium chloride successively, yields 4-hydroxyxanthone, melting at 241° (m. p. 224°, Kostanecki and Rutishauser, Abstr., 1892, 1096), and 4-methoxyxanthone, melting at 173° (m. p. 165°, Dreher and Kostanecki, Abstr., 1893, i, 1, 217).

2-Methoxyxanthone is formed by the action of concentrated sulphuric acid on the *p*-methoxyphenyl ether of salicylic acid, obtained by the condensation of *o*-chlorobenzoic acid with the monomethyl ether of quinol. G. Y.

Action of Bromine on certain Non-saturated Compounds. GALEAZZO PICCININI (*Atti R. Accad. Torino*, 1904—1905, **40**, 463—486).—Many unsaturated compounds are known which are stable towards bromine, and in these the carbon atoms connected by the double linking are generally attached to energetic electro-negative groups; the double linking itself confers a negative character on the carbon atoms on either side.

The author has investigated the action of bromine on certain unsaturated aromatic cyano-amides. He finds that the melting points of the bromo-derivatives prepared are higher than those of the amides themselves by an approximately constant amount. Also, ethyl bromomethylenedioxyphenyl-α-cyanoacrylate and ethyl bromodimethoxyphenyl-α-cyanoacrylate have melting points practically identical with those of the bromo-aldehydes to which they give rise on decomposition. Further, halogenated aromatic derivatives are decomposed by aqueous or alcoholic solutions of potassium hydroxide if the halogen is in the

side chain, whilst, if the halogen is in the benzene nucleus, reaction only takes place if it is near a nitro-group.

α-Cyano-β-piperonylideneacetamide melts at 212—213°, and not at 209° as previously stated (Abstr., 1904, i, 91); it is best prepared by condensing piperonaldehyde and cyanoacetamide in presence of glacial acetic acid or 15 per cent. aqueous ammonia. Its bromo-derivative, melting at 245° (*loc. cit.*), yields bromopiperonaldehyde when distilled with sodium hydroxide in a current of steam, so that the bromine atom must be in the benzene nucleus, the constitution being $CH_2<^{O}_{O}>C_6H_2Br\cdot CH\!:\!C(CN)\cdot CO\cdot NH_2$.

Bechert (Abstr., 1894, i, 489) has erroneously ascribed to a bromo-derivative, obtained from ethyl methylenedioxyphenyl-α-cyanoacrylate, and melting at 131°, the formula $CH_2O_2\!:\!C_6H_3\cdot CBr\!:\!C(CN)\cdot CO\cdot NH_2$; the author shows that its constitution is expressed by

$$CH_2O_2\!:\!C_6H_2Br\cdot CH\!:\!C(CN)\cdot CO_2Et.$$

p-Hydroxy-m-methoxyphenyl-α-cyanoacrylamide yields a *bromo-derivative*, $OH\cdot C_6H_2Br(OMe)\cdot CH\!:\!C(CN)\cdot CO\cdot NH_2$, which crystallises from alcohol in small, yellow leaflets melting and decomposing at 234—235°, and dissolves in acetic acid. On oxidation with chromic acid, it yields bromovanillin.

Dihydroxyphenyl-α-cyanoacrylamide yields a *bromo*-derivative, $C_6H_2Br(OH)_2\cdot CH\!:\!C(CN)\cdot CO\cdot NH_2$, which blackens at 230—235°, melts and decomposes at about 260°, and dissolves in dilute potassium hydroxide solution, giving a carmine solution turning yellow on boiling.

Ethyl 3 : 4-dimethoxyphenyl-α-cyanoacrylate yields a *bromo*-derivative, $C_6H_2Br(OMe)_2\cdot CH\!:\!C(CN)\cdot CO_2Et$, which crystallises from 90 per cent. alcohol in shining, pale yellow leaflets, melting at 154°, and is soluble in benzene, acetone, or boiling alkali solutions. When boiled with 10 per cent. sodium hydroxide solution, it is partially decomposed, yielding *bromoveratraldehyde*, $C_6H_3Br(OMe)_2\cdot CHO$, which can also be obtained by direct bromination of veratraldehyde, and crystallises from water in slender, colourless needles, melting at 151°; it gives a yellow, crystalline *phenylhydrazone*, reduces ammoniacal silver nitrate solution, and has the normal molecular weight in freezing benzene.

The bromo-derivative of ethyl cinnamenyl-α-cyanoacrylate, $CHPhBr\cdot CHBr\cdot CH\!:\!C(CN)\cdot CO_2Et$, melts at 100°, and not at 95° as stated by Bechert (*loc. cit.*); it has the normal molecular weight in freezing benzene, and when oxidised by means of chromic acid yields $\alpha\beta$-dibromo-β-phenylpropionic acid. T. H. P.

Hydrophthalic Acids: Two New Hydrophthalic Anhydrides I. GINO ABATI and LUIGI DE BERNARDINIS (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1905, [iii], 11, 61—70).—The reduction of sodium phthalate by sodium amalgam when heated yields the following two anhydrides: cis.Δ^3-*Tetrahydrophthalic anhydride*, $C_6H_8<^{CO}_{CO}>O$, which crystallises from water in shining, white scales, melting at 70°, and is readily soluble in alcohol or sodium carbonate solution; it has an acid reaction

towards litmus paper, and can be titrated with standard alcoholic potassium hydroxide solution; by heating at 220—230°, it is transformed into Δ^1-tetrahydrophthalic anhydride; when neutralised with sodium hydroxide, it is oxidised by permanganate, although less slowly than the tetrahydrophthalic acids. It gives a *dibromo*-derivative, $C_8H_{10}O_4Br_2$, which separates from aqueous alcohol in whitish crystals melting at 187°, and slowly reduces permanganate solution. With *p*-anisidine, it gives a *compound*, $C_6H_8<^{CO}_{CO}>N\cdot C_6H_4\cdot OMe$, which crystallises from alcohol in white leaflets, melting at 88°.

$\Delta^{1:3}$-*Dihydrophthalic anhydride*, $C_6H_6<^{CO}_{CO}>O$, crystallises from alcohol in shining, white scales melting at 58°, and is readily soluble in ether or benzene, and slightly so in water; it has an acid reaction towards litmus paper, and dissolves readily in sodium carbonate solution; when heated at about 225°, it is transformed into another anhydride, which could not be purified, but on treatment with *p*-anisidine in alcoholic solution yields an imide melting at 89°; it is not acted on by bromine or hydrobromic acid.

Besides the above anhydrides, the reduction of sodium phthalate by sodium amalgam gives a small quantity of a *substance* which melts at 174° and is probably a hydrophthalic acid; on boiling with acetic anhydride, it yields a crystalline product melting at 97—98°.

T. H. P.

Synthesis of α-Amino-acids by means of Ethyl Phthaliminomalonate. S. P. L. SÖRENSEN (*Zeit. physiol. Chem.*, 1905, **44**, 448—460. Compare Abstr., 1903, i, 833).—Various α-amino-acids have been synthesised by the action of different haloid derivatives on the sodio-derivative of ethyl phthaliminomalonate and subsequent hydrolysis with baryta and then with hydrochloric acid. Phenylalanine has been obtained from benzyl chloride, allylglycine from allyl iodide; ornithine from γ-bromopropylphthalimide (Abstr., 1888, 1292); α-aminoadipic acid from γ-chlorobutyronitrile (Abstr., 1890, 1221); αε-diaminopimelic acid from trimethylene bromide; αδ-diamino-adipic acid from ethylene bromide, and α-amino-δ-hydroxyvaleric acid by using a large excess of trimethylene bromide.

Full directions for the preparation of ethyl sodiophthaliminomalonate are given. Good yields of the synthetical products are only obtained when the condensation proceeds in the absence of alcohol, and it is essential that all the reagents should be free from water. J. J. S.

Synthesis of Aldehydes by means of Formic Acid. JOSEF HOUBEN (*Chem. Zeit.*, 1905, **29**, 667).—The author claims priority for his work over that of Zelinski on the same subject (*ibid.*, 1904, **28**, 303). As the result of a number of experiments, the following conditions were found to give the best yield of phenylacetaldehyde. A solution of 60 grams of benzyl chloride in 200 c.c. of ether, after treatment with 11·5 grams of magnesium, was slowly run into 10·9 grams of glacial formic acid dissolved in 100 c.c. of ether, the mixture being kept thoroughly shaken and cooled. After standing for 36 hours,

it was decomposed with ice and dilute sulphuric acid; the ethereal extract from this solution was shaken with sodium hydrogen sulphite, and the resulting compound, after decomposition with sodium carbonate and extraction with ether, yielded 5·3 grams of phenylacetaldehyde boiling at 204—209°. P. H.

Decahydro-β-naphthyl Ketone and Decahydro-β-naphthylamine. HENRI LEROUX (*Compt. rend.*, 1905, **141**, 46—47).—*Decahydro-β-naphthyl ketone*, $C_{10}H_{16}O$, prepared by oxidising decahydro-β-naphthol (this vol., i, 278) with chromic acid, is a colourless liquid with a strong, unpleasant odour; it boils at 116° under 15 mm. pressure, has a sp. gr. 0·988 at 0° and 0·979 at 16°, n_D 1·4834 at 16°, and is slightly soluble in water, readily so in alcohol and ether. The *sodium hydrogen sulphite* derivative crystallises from water in nacreous lamellæ. The *semicarbazone* separates from alcohol in slender needles and melts at 195°; the *phenylhydrazone* rapidly becomes coloured on exposure to air; the *oxime* forms small, colourless prisms and melts at 76° and on reduction with sodium and alcohol forms *decahydro-β-naphthylamine*, $C_{10}H_{17}\cdot NH_2$. This is a colourless liquid with an unpleasant odour, it distils at 112° under 15 mm. pressure, and is a strong base absorbing carbon dioxide from the air. The *hydrochloride* forms small, colourless prisms, and the *picrate* is crystalline and melts at 203—204°. T. A. H.

Action of a Mixture of Glacial Acetic Acid and Hydriodic Acid on Quinones. KASIMIR LAGODZINSKI (*Ber.*, 1905, **38**, 2301—2306. Compare Liebermann and Mamlock, this vol., i, 531). —When hydriodic acid of sp. gr. 1·70 is added to a boiling mixture of anthraquinone and glacial acetic acid, the anthraquinone dissolves and from the brown solution brown, glistening needles separate on cooling. When this *compound*, the constitution of which has not been determined, is warmed, iodine separates, the residue consisting of anthranol which melts at 154°; a similar change takes place when the solution of the compound in ether, benzene, or alcohol is heated. A mixture of glacial acetic acid and hydriodic acid appears to attack anthranol itself.

By the action of a mixture of glacial acetic acid and hydriodic acid on alizarin, red, glistening needles of a *compound* were obtained, whilst by the action on phenanthraquinone dark brown crystals of a *compound* separated. A. McK.

Camphoracetic and β-Camphorpropionic Acids. ALBIN HALLER (*Compt. rend.*, 1905, **141**, 13—16. Compare this vol., i, 533). —*Methyl carboxycamphoracetate*, $C_8H_{14}<\begin{matrix}C(CO_2Me)\cdot CH_2\cdot CO_2Me \\ | \\ CO\end{matrix}$, prepared by the action of methyl iodoacetate on methyl camphorcarboxylate in presence of sodium methoxide, is a yellow oil which boils at 194—196° under 15 mm. pressure, does not solidify above 0°, has $[\alpha]_D$ +65°42′ in alcohol, and is soluble in organic solvents but insoluble in water. When heated with potassium hydroxide in alcohol, it yields pot ssium camphoracetate, potassium carbonate, and methyl

alcohol, and with sodium ethoxide in alcohol, a viscous, uncrystallisable *acid* from which no homocamphoric acid could be isolated. *Camphoracetic acid*, $C_8H_{14}<\begin{matrix}CH\cdot CH_2\cdot CO_2H\\ |\\ CO\end{matrix}$, crystallises from boiling water in colourless, flattened needles, melts at 175°, and has $[\alpha]_D$ $+70°42'$ in alcohol. *Methylcarboxy-β-camphorpropionate*,

$$C_8H_{14}<\begin{matrix}C(CO_2Me)\cdot CH_2\cdot CH_2\cdot CO_2Me\\ |\\ CO\end{matrix},$$

prepared from methyl camphorcarboxylate and methyl β-iodopropionate, is a thick, yellow oil which boils at 200—204° under 10 mm. pressure, has $[\alpha]_D$ $+51°22'$, and is insoluble in water and alkalis but dissolves in most organic solvents. When hydrolysed with potassium hydroxide in alcohol or with dilute (10 per cent.) sulphuric acid, it yields *β-camphorpropionic acid*, $C_8H_{14}<\begin{matrix}CH\cdot CH_2\cdot CH_2\cdot CO_2H\\ |\\ CO\end{matrix}$. This is purified through the lead salt and then melts at 52—53°, has $[\alpha]_D$ $+45°35'$ in alcohol, and is readily soluble in alcohol or ether, and slightly so in water. These and previous results indicate that methyl camphorcarboxylate, unlike the sodium derivative of cyanocamphor, always behaves as a β-ketone towards alkyl iodides or iodo-esters.

T. A. H.

Alkylthujones and Compounds of Thujone (Tanacetone) with Aldehydes. ALBIN HALLER (*Compt. rend.*, 1905, **140**, 1626—1631. Compare Abstr., 1904, i, 600, and this vol., i, 214, and Semmler, Abstr., 1904, i, 176).—The alkylthujones were prepared by adding the appropriate alkyl iodide to a mixture of thujone and dry ether in which the requisite quantity of sodamide had been dissolved previously. The products are mobile liquids having odours resembling that of thujone. *Methylthujone*, $C_8H_{14}<\begin{matrix}CHMe\\ |\\ CO\end{matrix}$, boils at 90° under 16 mm. pressure and has $[\alpha]_D$ $16°16'$ at 15°, and a sp. gr. 0·9102 at 15°/4°; the *semicarbazone* crystallises from alcohol, melts at 164°, and re-melts at 183—184°. A small quantity of *dimethylthujone* is also formed. *Ethylthujone* distils at 93—96° under 13 mm. pressure, has $[\alpha]_D$ $-48°23'$ at 15°, and a sp. gr. 0·9155 at 15°/4° and yields a *semicarbazone*, which crystallises in small needles, melts at 131°, and re-melts at 171°. *Propylthujone* boils at 107—110° under 16 mm. pressure, has $[\alpha]_D$ $-48°28'$ at 15°, and a sp. gr. 0·9102 at 15°/4°; the *semicarbazone* resembles that of ethylthujone and melts at 164—168°. *Allylthujone* distils between 108° and 110° under 15 mm. pressure, has $[\alpha]_D$ $-50°47'$ at 15°, and a sp. gr. 0·9254 at 15°/4°, and furnishes a *semicarbazone*, which crystallises in needles, melts at 130—131°, and re-melts at 150—151°. It was observed that by the action of sodamide on thujone alone a reduction in the value of the rotatory power was produced, consequently no deductions as to the effect of the introduction of alkyl groups on the value of the rotatory power can be deduced from the specific rotations now recorded.

Benzylidenethujone, prepared by Semmler's process (Abstr., 1904, i, 176), has $[\alpha]_D$ $-590°8'$ in alcohol at 15°. *Anisylidenethujone*,

$C_8H_{14}<\begin{matrix}C:CH\cdot C_6H_4\cdot OMe \\ | \\ CO\end{matrix}$, crystallises in small, white needles, melts at 85°, boils at 223—224° under 14 mm. pressure, and has $[\alpha]_D$ −829°3′ in alcohol at 15°. *Piperonylidenethujone* crystallises in small, white scales which become yellow on exposure to light, melts at 114°, and has $[\alpha]_D$ −765° in alcohol at 15°. The high specific rotations of these substances afford further evidence of the influence of ethylenic linkings in increasing the values of this constant (compare Abstr., 1903, ii, 622).

*Piperonylidene*iso*thujone*, similarly prepared from *iso*thujone, crystallises in faintly yellow, flattened needles, melts at 131—132°, and is optically inactive. T. A. H.

Terpinene Nitrosite. T. AMENOMIYA (*Ber.*, 1905, 38, 2020—2021).—When nitric acid of sp. gr. 1·4 is warmed with a solution of terpinene nitrite in glacial acetic acid and the product poured into water, yellow crystals of the *compound* $C_{10}H_{15}O_6N_3$, melting at about 73°, are formed. By the action of aniline on it, the *compound* $C_{16}H_{21}O_4N_3$ is formed and separates from alcohol in yellow needles, melting at 145°. The reaction probably proceeds according to the equation $C_{10}H_{15}O_6N_3 + C_6H_7N = C_{16}H_{21}O_4N_3 + HNO_2$. A. McK.

Ginger Grass Oil. HEINRICH WALBAUM and O. HÜTHIG (*J. pr. Chem.*, 1905, [ii], 71, 459—473. Compare this vol., i, 53; Gildemeister and Stephan, Abstr., 1897, i, 81; Schimmel & Co., Abstr., 1904, i, 603; this vol., i, 536).—The constants for commercial ginger grass oil lie within the following limits: sp. gr. 0·9277—0·9458 at 15°; α_D −29°25′ + 22°40′; saponification number 0·9—3·2; saponification number after acetylation 130—172; ester number 9·5—24. The oil boils at 50—100° under 5·6 mm. pressure; the lowest boiling fractions contain *d*-α-phellandrene, dipentene, and *d*-limonene; the fractions boiling at 80—90° contain an aldehyde, $C_{10}H_{16}O$, which is isolated as the sodium hydrogen sulphite compound; the fraction boiling at 80—83·5° contains also *i*-carvone; whilst geraniol and dihydrocuminol are found principally in the fractions boiling at 85—95°.

The *aldehyde*, $C_{10}H_{16}O$, occurs in the ginger grass oil to the extent of about 0·2 per cent.; it is a colourless oil, with an odour resembling that of heptaldehyde or of citronellal, boils at 76—78° under 5 mm., or at 221—224° under 754 mm. pressure, has a sp. gr. 0·9351 at 15°, α_D ± 0°, and n_D 1·47348 at 20°. The *semicarbazone*, $C_{11}H_{19}ON_3$, melts at 169—170°; the *oxime* melts at 115—116°; the *phenylhydrazone* melts at 63°; the *semioxamazone* melts at 244—245°; the derivative with naphthacinchonic acid melts at 261°. The aldehyde is slowly oxidised on exposure to the air, more quickly by treatment with silver oxide, to the *acid* $C_{10}H_{16}O_2$, which crystallises in leaflets, melts at 106—107°, boils at 133—135° under 4 mm. pressure, and when treated with bromine in chloroform solution forms a *dibromide*, $C_{10}H_{16}O_2Br_2$; this crystallises in glistening leaflets and melts at 116—117°. The same acid is obtained on acidification of the product of alkaline hydrolysis from ginger grass oil. The *acetate*, obtained by reducing the aldehyde with zinc dust and glacial acetic acid, is a liquid with a fruity odour; it boils at 98—102° under 4 mm. pressure,

and on hydrolysis yields the *alcohol* $C_{10}H_{18}O$, which is a viscid oil having a pleasant odour. It boils at 89—91° under 4 mm., or at 236—238° under 755 mm. pressure, has a sp. gr. 0·9419 at 15°, $\alpha_D \pm 0°$, and n_D 1·48652 at 22°. The *phenylurethane*, formed by the action of phenylcarbimide on the alcohol, melts at 100—101°; the *diphenylurethane*, formed by the action of diphenylcarbamic chloride and pyridine on the alcohol, melts at 84—86°.

Geraniol and dihydrocuminol are separated partially by treatment with calcium chloride or with phthalic anhydride, as dihydrocuminol does not combine with either of these reagents; on the treatment of the impure dihydrocuminol with 90 per cent. formic acid, the remainder of the geraniol is converted into terpene or polyterpenes, whilst only a small fraction of the dihydrocuminol is converted into *p*-cymene. A lævorotatory ginger grass oil yielded dihydrocuminol which boils at 92—93·5° under 5 mm., or at 226—227° under 767 mm. pressure, and has a sp. gr. 0·9510 at 15°, α_D −13°18′, and n_D 1·49629 at 20°.

The *p*-cymene formed from dihydrocuminol boils at 175—176°, and has a sp. gr. 0·8608 at 15°, α_D +0·4°, and n_D 1·48935 at 20°. When dihydrocuminol is heated with zinc chloride or pyruvic acid, in addition to *p*-cymene, there is obtained a *product* which has an odour resembling that of pinol, boils at 185—200°, and forms a crystalline *additive* product with iodine melting at 169—170°.

Oxidation of dihydrocuminol with 4 per cent. potassium permanganate solution leads to the formation of terephthalic and *p*-hydroxy-*iso*propylbenzoic acids, but with 1 per cent. solution, to the formation of a *glycol* which could not be crystallised.

Dihydrocuminaldehyde, $C_{10}H_{14}O$, boils at 85° under 4 mm., or at 235° under 755 mm. pressure, and has a sp. gr. 0·9698 at 15°, α_D −37°54′, and n_D 1·50702 at 20°. The *semicarbazone* melts at 198—198·5°; the *semioxamazone* melts at 228°.

Dihydrocuminic acid, formed from dihydrocuminol, crystallises in leaflets and melts at 130—131°, but is not identical with Baeyer and Villiger's acid obtained from nopic acid (Abstr., 1896, i, 622), as it forms a *hydrobromide* melting at 175°. This is isomeric, and not identical with Baeyer and Villiger's bromotetrahydrocuminic acid (*loc. cit.*).

On acetylation of dihydrocuminol with acetic anhydride and distillation of the product, there was obtained a fraction containing 97·71 per cent. of the *acetate*, $C_{10}H_{15}O.Ac$; this boiled at 90—91° under 4 mm. pressure, and had a sp. gr. 0·9725 at 15°, α_D −4°30′, n_D 1·47615 at 20°, and an ester number 282.

Reduction of dihydrocuminol with sodium in amyl alcoholic solution leads to the formation of *tetrahydrocuminol* which boils at 79—80° under 5 mm. or at 216—218° under the ordinary pressure, has a sp. gr. 0·9419 at 15°, and forms a *phenylurethane*, $C_{17}H_{23}O_2N$, melting at 85—86°. G. Y.

Pyrogenetic Decomposition of Lac Resin. ALEXANDER ÉTARD and E. WALLÉE (*Compt. rend.*, 1905, **140**, 1603—1606).—When lac resin is submitted to destructive distillation, it furnishes 22 per cent. of a light "coke" apparently derived from starchy matter, 6 per cent. of

gas, 52 per cent. of a yellow oil, and 20 per cent. of an aqueous distillate. The oil contains, in addition to oleic acid and small quantities of hexoic and sebacic acids, the following neutral substances: a terpene, apparently of the dipentene group, boiling at 170—175°; a terpenic hydrocarbon which is greenish-blue in colour and boils at 235—240°; a paraffin, $C_{32}H_{66}$, which crystallises in colourless spangles, melts at 61—62°, boils at 360°, and resembles the hydrocarbons found in association with chlorophyll; and a polyterpene which boils at 310°. These results indicate that lac resin may be composed of a series of unstable oleates of polyterpenes. T. A. H.

Brazilin and Hæmatoxylin. JOSEF HERZIG and JACQUES POLLAK (*Ber.*, 1905, **38**, 2166—2168. Compare Abstr., 1903, i, 270, 713; 1904, i, 81, 908; Gilbody and Perkin, Trans., 1902, **81**, 1040).—Trimethylbrazilone, when heated on the water-bath with an excess of phenylhydrazine and glacial acetic acid, yields a *phenylhydrazine* derivative, $C_{22}H_{13}ON_2(OMe)_3$. It crystallises from ethyl acetate in slender, yellow needles, melts at 239—242°, and cannot be acetylated. At higher temperatures, the product is Gilbody and Perkin's deoxytrimethylbrazilone, which melts at 165—168° and not at 173°.

No corresponding nitrogen derivative has so far been obtained from tetramethylhæmatoxolone. When this compound is heated on the water-bath with glacial acetic acid and phenylhydrazine, the product is *deoxytetramethylhæmatoxolone*, $C_{16}H_{18}O(OMe)_4$. It crystallises from benzene in colourless needles and melts at 170—175°. J. J. S.

Oxonium and Ammonium Salts. ARTHUR HANTZSCH (*Ber.*, 1905, **38**, 2143—2154).—Electrical conductivity determinations of dimethylpyrone hydrochloride and sulphate indicate that these salts are practically completely hydrolysed in aqueous solution. The values for solutions of the salts are smaller than the conductivity values for solutions of the free acid of equivalent strength, especially in the case of concentrated solutions of the sulphate. This is not attributed to the presence of definite amounts of pyronium salt in the solution, since sucrose, chloral hydrate, and dextrose produce a similar lowering on the conductivity of solutions of hydrochloric and sulphuric acids.

Oxonium salts of the type $C_6H_4{<}{}^{R-}_{OX}{>}C_6H_4$ or $C_6H_4{<}{}^{R-}_{\mid\,OX}{>}C_6H_4$ are somewhat more stable but are also readily decomposed by water. The tendency of quadrivalent oxygen to form salts and bases is thus extremely small compared with the same tendency of quinquevalent nitrogen. Attempts have been made to distinguish between Bernthsen's ammonium, $NH_2Cl{:}C_6H_3{<}{}^{N}_{S}{>}C_6H_4$, and Kehrmann's thionium formula, $NH_2{\cdot}C_6H_3{<}{}^{N-}_{SCl}{>}C_6H_4$, for thiazine dyes and corresponding oxazine salts (Abstr., 1902, i, 566). Kehrmann's observations on the readiness with which the bases can be diazotised are not regarded as incompatible with the ammonium formula. All these salts are much more stable than the oxonium salts, but no conductivity determinations could be made on account of the fact that they are so sparingly soluble. As examples of soluble aminophenaz-

thionium salts, methylene-blue and Lauth's-violet, and of soluble aminophenoxazonium salts, Meldola's blue, have been selected. The results of conductivity determinations show that the salts are not hydrolysed to any appreciable extent, in fact to about the same extent as ammonium or potassium chloride, and the values obtained, especially with Meldola's blue, correspond closely with those previously given for pararosanilinium chloride (Hantzsch and Osswald, Abstr., 1900, i, 256). The conductivities of solutions obtained by mixing the above salts with equivalent amounts of sodium hydroxide have been determined. With Meldola's blue, the colour is almost instantaneously destroyed and the value for the conductivity is practically that of pure sodium chloride of equivalent concentration, thus indicating that the ammonium base is instantaneously isomerised to the phenol

$$NMe_2{\cdot}C_6H_3{<}{\overset{NH}{\underset{O}{}}}{>}C_6H_3{\cdot}OH.$$

The base from Lauth's-violet is somewhat more stable, and the value of the conductivity falls to that of sodium chloride only after some 28 hours. The methylene-blue base, on the other hand, is perfectly stable; the conductivity of the solution obtained on the addition of an equivalent of alkali to its salts remains constant, $v = 256$, μ for ammonium base $= 148$, since the ammonium base cannot undergo intramolecular rearrangement.

The conclusion is drawn that on the whole the facts are more in harmony with the ammonium than with the oxonium and thionium formulæ for the oxazine and thiazine dyes, since it is difficult to see why the introduction of amino-groups into an extremely unstable oxonium or thionium salt should render it as stable and as little hydrolysed as ammonium chloride. Similar arguments are used with reference to carbonium salts, and in reply to Baeyer (this vol., i, 281) it is pointed out that the coloured sulphate from colourless *p*-trihalogen triphenylcarbinol may have an ortho-quinonoid structure although a para-quinonoid formula is impossible. J. J. S.

Fisetin Derivatives containing less Oxygen. J. Berstein, C. Fraschina and Stanislaus von Kostanecki (*Ber.*, 1905, **38**, 2177—2182).—2'-*Hydroxy*-3 : 4-*dimethoxychalkone*, prepared by condensing veratraldehyde with *o*-hydroxyacetophenone, crystallises from alcohol in orange-yellow plates melting at 115°. The alcoholic solution, when heated with hydrochloric acid, is converted into 3' : 4'-*dimethoxyflavanone*, which crystallises in colourless plates melting at 123—125°, dissolves in alcoholic sodium hydroxide with an orange yellow, and in sulphuric acid with an orange-red, coloration. 3-*Bromo*-3' : 4'-*dimethoxyflavanone*, prepared by bromination in disulphide solution, forms colourless prisms which melt and decompose at 160°. 3' : 4'-*Dimethoxyflavone*, formed by the action of concentrated potassium hydroxide on the preceding compound, separates from alcohol in colourless needles melting at 154—155°; it dissolves in sulphuric acid with a yellow coloration, and the dilute alcoholic solution has an intensely violet fluorescence.

3'-4'-*Dihydroxyflavone* crystallises in bright yellow prisms melting at 243°; it dyes cotton yarn bright yellow with aluminium mordants and

grey to black with iron mordants. 3′ : 4′-*Diacetoxyflavone*, $C_{15}H_8O_2(OAc)_2$, crystallises in colourless, glistening needles melting at 171°. 3-*Isonitroso*-3′ : 4′-*dimethoxyflavanone*, prepared by the action of amyl nitrite and hydrogen chloride on the dimethoxyflavanone, crystallises from benzene in colourless rosettes of needles ; it gives orange-yellow shades with cobalt mordants.

3′ : 4′-*Dimethoxyflavonol* crystallises in large, yellow needles, melts at 199—200°, and gives an intense yellow coloration with sulphuric acid ; it forms a sparingly soluble yellow *sodium* salt. *Acetyl*-3′ : 4′-*dimethoxyflavonol*, $OAc\cdot C_{15}H_7O_2(OMe)_2$, separates from dilute alcohol in long, colourless needles melting at 130—131°. 3′ : 4′-*Dihydroxyflavonol* results from the action of hydrogen iodide on the foregoing ; it crystallises in short, broad, yellow needles melting and decomposing at 303°, gives a yellowish-red coloration with sodium hydroxide, and dyes orange-yellow with aluminium and grey to black with iron mordants. *Acetyl*-3′ : 4′-*diacetoxyflavonol* forms colourless needles melting at 199—200°. The whole of the 14 hydroxy-derivatives of flavone have now been described. E. F. A.

Pyranic [Xanthyl] Phenols. Robert Fosse and A. Robyn (*Compt. rend.*, 1905, **140**, 1538—1540. Compare Abstr., 1904, i, 83, 336).—The dinaphthaxanthyl phenols already described are insoluble in aqueous, but soluble in alcoholic, alkali hydroxides. This anomalous behaviour of the hydroxyl group is probably due to an intermolecular neutralisation, the compound being an oxygen salt having the formula

$$\begin{array}{l} CH{<}^{C_{10}H_6}_{C_{10}H_6}{>}O \\ | \qquad\qquad\quad \| \\ R\text{———————}OH \end{array} \quad \text{or} \quad \begin{array}{l} CH{<}^{C_{10}H_6}_{C_{10}H_6}{>}OH \\ | \qquad\qquad\quad | \\ R\text{———————}O \end{array}.$$

In the present paper, the condensation products of dinaphthaxanthonium salts with resorcinol, pyrogallol, and *m*-diethylaminophenol are described. 1 : 3-*Dihydroxy*-4 : 6-bis*dinaphthaxanthyl benzene*,

$$CH{<}^{C(OH)\cdot C(C_{21}H_{13}O)}_{C(OH):C(C_{21}H_{13}O)}{>}CH,$$

obtained from dinaphthaxanthonium bromide and resorcinol, crystallises from ethyl acetate, decomposes without melting, and is insoluble in aqueous, but soluble in alcoholic, alkali hydroxides ; the *diacetyl* derivative forms small, white crystals, which decompose without previous fusion. 1 : 3 : 5-*Trihydroxy*-2 : 4 : 6-*tridinaphthaxanthyl benzene*,

$$O:(C_{10}H_6)_2:CH\cdot C{<}^{C(OH)\cdot C(C_{21}H_{13}O)}_{C(OH):C(C_{21}H_{13}O)}{>}C\cdot OH,$$

crystallises from acetic acid in beautiful, colourless needles, decomposes without fusion, is soluble in alcoholic, and insoluble in aqueous alkali hydroxides ; it yields a *triacetate*, which melts at 270° and crystallises from toluene in beautiful, white crystals. 1 : 5-*Dihydroxy*-2-*dinaphthaxanthylbenzene*, $OH\cdot C_6H_3\cdot C_{21}H_{13}O$, decomposes below 300°, is soluble in aqueous alkali hydroxides, and yields a *diacetyl* derivative which melts at 230—231° and crystallises from toluene in white crystals. 1-*Hydroxy*-3-*diethylamino*-4 : 6-bis*dinaphthaxanthyl benzene*, $OH\cdot C_6H_2(C_{21}H_{13}O)_2\cdot NEt_2$, obtained from dinaphthaxanthonium bromide and *m*-diethylaminophenol, forms small crystals becoming

violet, melts at 250—252°, and is soluble in alcoholic but insoluble in aqueous alkali hydroxides. M. A. W.

Dinaphthapyranic [Dinaphthaxanthyl] Derivatives containing Nitrogen. A. Robyn (*Compt. rend.*, 1905, **140**, 1644. Compare Fosse, Abstr., 1904, i, 337).—*Aminophenyldinaphthaxanthen*,

$$NH_2\cdot C_6H_4\cdot CH{<}{}^{C_{10}H_6}_{C_{10}H_6}{>}O,$$

prepared by condensing aniline with dinaphthaxanthonium hydrobromide (*loc. cit.*), forms colourless crystals, melts and decomposes at 250—253°, is soluble in benzene and insoluble in alcohol. o-*Aminotolyldinaphthaxanthen*, similarly prepared, resembles the foregoing and melts at 270—271°; the *isomeride* derived from *p*-toluidine melts at 232—233°. m-*Aminotolylbisdinaphthaxanthen*,

$$NH_2\cdot C_7H_5\left[CH{<}{}^{C_{10}H_6}_{C_{10}H_6}{>}O\right]_2,$$

melts at 275° and is less soluble in benzene than the foregoing. *a-Naphthylaminodinaphthaxanthen* forms slightly coloured crystals and melts at 255—260°. T. A. H.

Action of Methyl Iodide on Sparteine. Charles Moureu and Amand Valeur (*Compt. rend.*, 1905, **140**, 1601—1603. Compare Abstr., 1903, i, 717; 1904, i, 187; Wackernagel and Wölffenstein, 1903, i, 917; Willstätter and Marx, 1904, i, 613; Semmler, 1904, i, 685; Scholtz and Pawlicki, 1904, i, 1045).—When a mixture of sparteine, methyl iodide, and methyl alcohol after remaining for 24 hours is heated for one hour, a mixture of two methiodides is produced. α-Sparteine methiodide is identical with Bamberger's substance (Abstr., 1887, 163); *α′-sparteine methiodide* was not obtained free from the α-isomeride, but is distinguished from it in being more soluble in water and in having a higher specific rotation, $[\alpha]_D$ $-36\cdot9°$.

The formation of sparteine methiodide hydriodide in Scholtz and Pawlicki's experiments is due to the liberation of hydrogen iodide by the interaction of the methyl iodide and methyl alcohol used. In this case hydriodides of the two isomeric methiodides are formed. The salt of the α-methiodide has $[\alpha]_D$ $-17\cdot1°$ in water, and the best preparation of the hydriodide of the α′-isomeride obtained had $[\alpha]_D$ $-46\cdot3°$. A small quantity of sparteine hydriodide $[\alpha]_D$ $-11\cdot06°$ in methyl alcohol) is also formed in this reaction. T. A. H.

Stereoisomerism of Sparteine Methiodides. Charles Moureu and Amand Valeur (*Compt. rend.*, 1905, **140**, 1645—1647).—When either of the two isomeric sparteine methiodide hydriodides produced by Scholtz and Pawlicki's process (Abstr., 1904, i, 1045, and preceding abstract) is heated, it yields methyl iodide and sparteine hydriodide, the only difference being that the α′-isomeride undergoes this decomposition at a slightly lower temperature than the salt of the α-methiodide. Further, when sparteine hydriodide is heated with excess of methyl iodide at 136° a mixture of the two sparteine methiodide hydriodides is formed. These observations indicate that these two substances are stereoisomerides, and that in both salts the methyl

iodide is attached to the same nitrogen atom and the hydrogen iodide to the other. T. A. H.

Action of Ethyl Iodide on Sparteine. CHARLES MOUREU and AMAND VALEUR (*Compt. rend.*, 1905, **141**, 49—51. Compare Scholtz and Pawlicki, Abstr., 1904, i, 1045, and preceding abstracts).—When sparteine reacts with ethyl iodide in the absence of any solvent, sparteine hydriodide is formed and ethylene liberated. When ethyl alcohol is employed as a solvent, the reaction proceeds slowly in the cold, and more rapidly on heating in a reflux apparatus or in closed tubes. In the last two cases the products are sparteine hydriodide and two isomeric sparteine ethiodides partly free and partly in the form of their hydriodides. One of the sparteine ethiodides crystallises in truncated tetrahedra, is slightly soluble in cold water and more soluble in warm water or methyl alcohol, and has $[\alpha]_D$ $-25°42'$ in methyl alcohol. The *hydriodide* of this form crystallises from a mixture of methyl alcohol and acetone and has $[\alpha]_D$ $-16°8'$ in water, and on treatment with alkalis yields sparteine ethiodide, not sparteine as Bamberger supposed (Abstr., 1887, 163). The isomeric *ethiodide* is very soluble in cold water and has $[\alpha]_D$ $-38°4'$.

The sparteine ethiodide hydriodide obtained by Mills and later by Bamberger (*loc. cit.*) is probably a mixture of the salts of the two isomeric ethiodides.

Ethyl iodide does not combine with sparteine hydriodide.

T. A. H.

Condensation of Nitromethane with Derivatives of Alkylated Aminomethyl Alcohol. LOUIS HENRY (*Ber.*, 1905, **38**, 2027—2031).—When nitromethane is condensed with 1-hydroxymethylpiperidine, the compound formed has the formula

$$NO_2\cdot CH(CH_2\cdot C_5NH_{10})_2,$$

and not $NO_2\cdot C(CH_2\cdot C_5NH_{10})_3$ as was formerly supposed by the author (*Bull. Acad. roy. Belg.*, 1896, [iii], **32**, 33).

The *compound* $NO_2\cdot CH(CH_2\cdot NMe_2)_2$, formed by the condensation of nitromethane with dimethylaminomethyl alcohol, crystallises in nacreous leaflets and melts at 56—57°.

The *compound* $OH\cdot CH_2\cdot C(CH_2\cdot C_5NH_{10})_2\cdot NO_2$, formed by the action of formaldehyde on the compound $NO_2\cdot CH(CH_2\cdot C_5NH_{10})_2$, melts at 101—102°. It may also be formed by the action of piperidine (1 mol. or 2 mols.) on the product resulting from the action of formaldehyde (3 mols.) on nitromethane (1 mol.) or by the action of 1-hydroxymethylpiperidine on nitroethyl alcohol. An *isomeride*, melting at 78—79° and crystallising from ether in needles, is formed when the former compound is submitted to further treatment with a solution of piperidine in hot alcohol. A. McK.

Isomeric Oxypyridines from β-Ketones. GIOVANNI ISSOGLIO (*Atti R. Accad. Sci. Torino*, 1904—1905, **40**, 493—506. Compare Guareschi, Abstr., 1900, i, 52).—In presence of ammonia, the β-ketones condense with ethyl cyanoacetate, yielding cyanopyridones (Guareschi, *loc. cit.*); and where the condensed radicles are identical only one com-

pound is obtained, but where these radicles are different two isomeric compounds may be obtained, the isomerism depending on the two different positions which the carbonyl groups may assume in the condensation. The author has examined the products obtained with benzoylacetone and with acetylmethyl hexyl ketone, and by distillation with zinc dust has been able to establish their constitutions.

The condensation of benzoylacetone with ethyl cyanoacetate in presence of ammonia yields: (1) benzoylacetonamine or benzoylacetonimine, formed by the action of ammonia on benzoylacetone; (2) 5-*cyano*-6-*oxy*-4-*phenyl*-2-*methyldihydropyridine*, $CPh\leqslant\begin{smallmatrix}CH_2-CMe\\C(CN)\cdot CO\end{smallmatrix}\geqslant N$, which crystallises from alcohol in slender, white, anhydrous needles melting at 263—264°, and dissolves slightly in water or acetone; (3) 5-*cyano*-6-*oxy*-2-*phenyl*-4-*methyldihydropyridine*, $CMe\leqslant\begin{smallmatrix}CH_2-CPh\\C(CN)\cdot CO\end{smallmatrix}\geqslant N$, which crystallises from alcohol in shining, nacreous plates exhibiting a slight blue fluorescence and melting at 310°; it is sparingly soluble in water, and, like the preceding compound, is soluble in dilute alkali hydroxide solutions, from which it is reprecipitated on acidification. They both reduce potassium permanganate energetically, hydrogen cyanide being evolved.

The condensation of acetylmethyl hexyl ketone with ethyl cyanoacetate in presence of ammonia yields: (1) 5-*cyano*-6-*oxy*-2-*methyl*-4-*hexylpyridine*, $C_6H_{13}\cdot C\leqslant\begin{smallmatrix}CH_2-CMe\\C(CN)\cdot CO\end{smallmatrix}\geqslant N$, which crystallises in large, shining plates having a soapy feel and melting at 108°, and is soluble in alcohol, ether, acetone, or benzene; (2) 5-*cyano*-6-*oxy*-4-*methyl*-2-*hexylpyridine*, $CMe\leqslant\begin{smallmatrix}CH_2\cdot C(C_6H_{13})\\C(CN)\text{——}CO\end{smallmatrix}\geqslant N$, which crystallises from aqueous alcohol in slender needles melting at 193—194°, dissolves in alcohol, ether, acetone, or benzene, and when powdered in a mortar readily becomes electrified.

From the above results the author concludes: (1) that a β-diketone containing two different radicles, on condensation with ethyl cyanoacetate in presence of ammonia, yields two well-defined isomerides; that the melting point and solubility of these compounds rise as the radicle with the higher molecular weight approaches the nitrogen atom; that with an equal number of carbon atoms the more highly hydrogenated oxypyridines have the lower melting points.

T. H. P.

Action of Formaldehyde on 1 : 2-Dimethyl-Δ^2-tetrahydropyridine. ANDREAS LIPP and EDUARD WIDNMANN (*Ber.*, 1905, **38**, 2276—2283. Compare Lipp, Abstr., 1892, 1244; 1897, i, 229; Lipp and Richard, Abstr., 1904, i, 342; Ladenburg, Abstr., 1893, i, 426; 1898, i, 687).—The base obtained by the condensation of formaldehyde with 1 : 2-dimethyl-Δ^2-tetrahydropyridine, reduction of the product with sodium and alcohol, elimination of water by the action of hydrochloric acid, and reduction of the resulting vinyl derivative with tin and hydrochloric acid, is identical with 1-methyl-3-ethylpiperidine formed from Stoehr's 3 ethylpiperidine (Abstr.,

1892, 628) by treatment with methyl iodide, conversion of the methiodide into the methochloride, and distillation of this at 240—250°. The properties of the bases prepared by these two series of reactions, and of the hydrochloride obtained from them, agree with those given for 1-methyl-3-ethylpiperidine and its hydrochloride by Ladenburg (Abstr., 1898, i, 688). The following salts were prepared from the bases of both origins: the aurichloride crystallises in sheaves of long needles and melts at 100—101° (m. p. 104—105°; Ladenburg, *loc. cit.*); the platinichloride, $(C_7H_{14}NMe)_2,H_2PtCl_6$, crystallises in orange-red, glistening prisms and melts at 145—148°; the *mercurichloride*, $(C_7H_{14}NMe,HCl)_2,3HgCl_2$, forms long, glistening needles and melts at 91—92°; the *picrate*, $C_8H_{17}N,C_6H_3O_7N_3$, crystallises in long needles and melts at 133—134°; the *methiodide*, $C_7H_{14}NMe,MeI$, crystallises in glistening octahedra or matted needles, and melts at 194—195° or at 197—198°; a mixture of the two methiodides of different genesis melted at 195—196°; the *methochloride* crystallises in stellate groups of needles and is deliquescent; the *aurichloride* of the methochloride, $C_7H_{14}NMe,MeCl,AuCl_3$, forms glistening, yellow leaflets and melts at 135—137°; the *platinichloride* of the methochloride, $(C_7H_{14}NMe,MeCl)_2,PtCl_4$, crystallises in glistening needles or prisms and melts and decomposes at 250° or at 255°. G. Y.

Indoline. GIUSEPPE PLANCHER and C. RAVENNA (*Atti R. Accad. Lincei*, 1905, **14**, i, 632—637).—*Indoline*, $C_6H_4<{CH_2 \atop NH}>CH_2$, prepared by heating 1-methylindoline in a sealed tube with phosphorus and hydriodic acid at 210—230°, is a colourless, faintly-smelling base lighter than water and boils at 220—221°; it can be kept for a long time without change, and in dilute sulphuric acid solution gives no coloration with nitrous acid. Its *picrate*, $C_{14}H_{12}O_7N_4$, separates from alcohol in minute crystals melting at 174°; its *hydrochloride* was prepared, and its *platinichloride*, $(C_8H_9N)_2,H_2PtCl_6$, which forms a yellow precipitate afterwards turning red, and decomposes without melting at about 180°; its *acid oxalate*, $C_{10}H_{10}O_4N$, separates from alcohol in colourless crystals melting at 128°.

1-*Benzoylindoline*, $C_{15}H_{13}O_2N$, separates from ethyl acetate in colourless, refractive, prismatic crystals melting at 118—119°.

1-*Nitrosoindoline*, $C_8H_8ON_2$, crystallises from light petroleum in faintly yellow scales melting at 83—84°, and exhibits normal cryoscopic behaviour in benzene solution; it gives the nitrosoamine reactions with Liebermann's reagent and with a sulphuric acid solution of diphenylamine, and, when treated with hydroxylamine hydrochloride, yields the original indoline. T. H. P.

Synthesis of Quinoline Derivatives. III. Action of Ethyl Benzoylacetate on Anthranilic Acid. STEFAN VON NIEMENTOWSKI (*Ber.*, 1905, **38**, 2044—2051. Compare Abstr., 1894, i, 427; 1896, i, 187).—Ethyl 4-hydroxy-2-phenylquinoline-3-carboxylate,

$$C_6H_4<{C(OH):C\cdot CO_2Et \atop N=\!=\!=\!=CPh},$$

is the main product obtained when anthranilic acid and ethyl benzoylacetate in molecular proportion are heated for 50 hours at 140—150°. It forms rectangular rods and melts and decomposes at 262°. The *compound* $C_{32}H_{20}O_5N_2$ is obtained as a by-product, which crystallises in yellow needles and melts at 308°.

When the condensation of ethyl benzoylacetate with anthranilic acid is conducted for 250 hours, the temperature finally being raised to 180°, *s*-triphenylbenzene, $C_{24}H_{18}$, crystallising in yellow needles and melting at 171°, is one of the products. Its formation is expressed by the equation $3CH_2Bz \cdot CO_2Et = C_{24}H_{18} + 3CO_2 + 2EtOH$. Ethyl 4-hydroxy-2-phenylquinoline-3-carboxylate is also formed in small yield in this case. A. McK.

A New Class of Quinoline Dyes. II. Emil Besthorn and J. Ibele (*Ber.*, 1905, **38**, 2127—2129. Compare Abstr., 1904, i, 527).—The red dye previously described may be prepared by the action of the chloride of quinaldinic acid on quinoline in dry benzene solution. The chloride of quinaldinic acid, obtained by the action of thionyl chloride, crystallises from light petroleum in needles, melts and turns brown at 97—98° and not at 175—177° as stated by H. Meyer (this vol., i, 155). It dissolves readily in ether or benzene and when boiled with water yields a red dye. J. J. S.

***iso*Nitrosomethyl*iso*oxazolone.** Louis Bouveault and André Wahl (*Ber.*, 1905, **38**, 2066—2067).—A reply to Hantzsch (this vol., i, 408).—The authors confirm Jovitschitsch's results (Abstr., 1896, i, 82), which contradict those of Nussberger (Abstr., 1892, 1175). When recrystallised from water, *iso*nitrosomethyl*iso*oxazolone forms anhydrous leaflets and melts at 159°. G. Y.

Derivative of Glycuronic Acid and *p*-Nitrophenylhydrazine. A Correction. An. K. Medvedeff (*Ber.*, 1905, **38**, 2283. Compare this vol., i, 491).—The compound $C_{18}H_{22}O_5N_6$, described in the previous paper, is now found to be the *p*-nitrophenylhydrazone of acetaldehyde. G. Y.

Synthesis of 5-Nitro-4-ketodihydroquinazolines from 6-Nitro-2-aminobenzoic Acid, 6-Nitro-2-acetylaminobenzoic Acid, and from the corresponding Nitroacetylanthranil. Marston T. Bogert and Victor J. Chambers (*J. Amer. Chem. Soc.*, 1905, **27**, 649—658).—6-Nitro-2-aminobenzoic acid is best prepared by the action of potassium hypobromite on 3 : 1-nitrophthalamic acid as described by Kahn (Abstr., 1903, i, 94). When the acid is boiled with excess of acetic anhydride, 6-*nitroacetylanthranil*,

$$NO_2 \cdot C_6H_3 < \begin{matrix} NAc \\ | \\ CO \end{matrix},$$

is produced which crystallises in large, colourless plates or prisms, melts at 155—156° (corr.), is soluble in acetone or hot chloroform, and reacts readily with primary amines to form substituted anthranilamides which easily condense to quinazolines.

6-*Nitro-2-acetylaminobenzoic acid*, $NO_2 \cdot C_6H_3(NHAc) \cdot CO_2H$, obtained by adding nitroacetylanthranil to boiling water, forms large prismatic

crystals, melts and decomposes at 212—214°, and is soluble in water, acetone, or hot alcohol, and slightly so in warm chloroform or benzene.

5-*Nitro-4-ketodihydroquinazoline*, $\begin{array}{l}\mathrm{CH{\cdot}CH{=\!=}C{\cdot}N{=}CH} \\ \mathrm{CH{\cdot}C(NO_2){:}C{\cdot}CO{\cdot}NH}\end{array}$, obtained by heating ammonium 6-nitro-2-aminobenzoate with formamide at 150—160°, crystallises in colourless needles, melts and decomposes at 255—256° (corr.), and is soluble in hot water, alcohol, or acetone. The colourless needles which separate from a hot aqueous solution gradually change into pale green prisms of the same melting point and solubility, the change being complete in 24—36 hours. The *hydrochloride*, *platinichloride*, and *nitrate* are described.

5-*Nitro-4-keto-2-methyldihydroquinazoline*, $\begin{array}{l}\mathrm{CH{\cdot}CH{=\!=}C{\cdot}N{=}CMe} \\ \mathrm{CH{\cdot}C(NO_2){:}C{\cdot}CO{\cdot}NH}\end{array}$, may be prepared by heating 6-nitro-2-aminobenzoic acid with acetic anhydride and acetonitrile in a sealed tube for 6 hours at 160—170°. It can also be obtained by the action of heat on ammonium 6-nitro-2-acetylaminobenzoate, or by dissolving nitroacetylanthranil in dilute ammonia and acidifying the solution with acetic acid. The compound crystallises from alcohol in slender, colourless needles, melts and decomposes at 277—279° (corr.), and is soluble in warm acetone or alcohol and slightly so in hot water; the *chloride* and *nitrate* are described.

5-*Nitro-4-keto-3-phenyl-2-methyldihydroquinazoline*,

$$\begin{array}{l}\mathrm{CH{\cdot}CH{=\!=}C{\cdot}N{=}CMe} \\ \mathrm{CH{\cdot}C(NO_2){:}C{\cdot}CO{\cdot}NPh}\end{array},$$

obtained by heating nitroacetylanthranil with excess of aniline and boiling the product with water acidified with acetic acid, crystallises from alcohol in cubes, melts at 233—234° (corr.), and is easily soluble in warm acetone or hot nitrobenzene. E. G.

New Series of Dihydroquinoxalines. JOHN B. EKELEY and ROBERT J. WELLS (*Ber.*, 1905, **38**, 2259—2264).—2-*Methyl*-3-iso-*propyl*-1:4-*dihydroquinoxaline*, $C_6H_4<\begin{array}{l}\mathrm{NH{\cdot}CMe} \\ \mathrm{NH{\cdot}CPr^{\beta}}\end{array}$, is formed by the action of hydrogen chloride on a mixture of *o*-phenylenediamine and acetone or mesityl oxide, or by heating *o*-phenylenediamine and mesityl oxide with phosphorus pentachloride at 160°, or when the diamine and mesityl oxide are heated together in molecular amounts in benzene; the free base is obtained from its hydrochloride by treatment with aqueous alkali hydroxides. It crystallises in large, monoclinic prisms or large, thin leaflets, melts at 124°, and dissolves in alcohol, ether, chloroform, carbon disulphide, hydrocarbons, or acids to colourless solutions which become yellow on warming. The *hydrochloride*, $C_{12}H_{16}N_2,2HCl$, and the *hydrobromide*, $C_{12}H_{16}N_2,2HBr$, are obtained in long, colourless needles on evaporation of their aqueous solutions, but on addition of the hydrogen haloids to benzene solutions of the base, lemon-yellow crystalline powders are obtained, the hydrobromide having the constitution $C_{12}H_{16}N_2,HBr$. The *sulphate* is very soluble in water, and on evaporation of its solution decomposes into mesityl oxide and *o*-phenylenediamine sulphate. The *picrate*, $C_{12}H_{16}N_2,2C_6H_3O_7N_3$, forms yellow crystals; the *platinichloride*, $(C_{12}H_{16}N_2)_2,H_2PtCl_6$, is

yellow. With sodium nitrite in glacial acetic acid solution, the base forms a *dinitroso*-derivative, $C_{12}H_{14}N_2(NO)_2$, which crystallises from ether in yellow needles, melts at 177°, and gives Liebermann's nitroso-reaction. The *dibenzoyl* derivative crystallises in small, yellow needles, softens at 85—90°, and decomposes at about 175°. The base is not reduced by sodium and boiling alcohol; with oxidising agents it yields a quinoxaline and sometimes a green fluorescent dihydroquinoxaline. With mercuric chloride the base forms a yellow, with copper sulphate a light green, precipitate.

o-Xylylenediamine, but not *o*-tolylenediamine, reacts with mesityl oxide to form a 1 : 4-dihydroquinoxaline. G. Y.

Laws of Substitution in Aromatic Compounds. Bernhard Flürscheim (*J. pr. Chem.*, 1905, [ii], **71**, 497—539. Compare Abstr., 1903, i, 79; Holleman, Abstr., 1903, i, 623; Kauffmann, Abstr., 1903, ii, 401).—The author replies to the criticisms of Holleman and of Kauffmann, and extends the application of the ideas underlying his law of substitution, to the formation of 1 : 4-additive compounds by substances containing conjugated ethylene linkings, to the constitution of triphenylmethyl, and to the formation of stereoisomerides.

The formation of azoxy-compounds by the reduction of nitro-compounds is preceded by the formation of an additive compound by the hydroxylamine and nitroso-compound which are the primary reduction products. The formation of the additive compound cannot take place if the nitrogen atom of the hydroxylamine is already pentavalent owing to salt formation, which, and not the velocity of the reduction (compare Goldschmidt and Ingebrechtsen, Abstr., 1904, ii, 608), is the cause of the non-appearance of azoxy-, azo-, or aminoazo-benzene in the reduction of nitrobenzene in acid solution. If negative groups are introduced into the benzene nucleus, as in *m*-dinitrobenzene, *s*-trinitrobenzene, or di-*m*-chloro-*p*-bromonitrobenzene, the hydroxylamine salt formed on reduction in acid solution is more or less dissociated, the additive compound is formed to a corresponding extent, and the reduction product is a mixture of the azoxy-, azo-, aminoazo-, and amino-compounds. The reduction of ethyl *m*-nitrobenzenesulphonate with stannous chloride and hydrochloric acid leads to the formation of the amine only, whilst under the same conditions *m*-nitrobenzenesulphonic chloride yields *m*-nitrobenzenesulphinic acid.

Di-m-*chloro*-p-*bromonitrobenzene*, $C_6H_2Cl_2Br{\cdot}NO_2$, is formed by the action of hydrogen bromide and sodium nitrite on 2 : 6-dichloro-4-nitroaniline in warm glacial acetic acid solution; it is colourless, melts at 87—88°, and is only slightly volatile in a current of steam.

3 : 3′ : 5 : 5′-*Tetrachloro*-4 : 4′-*dibromoazoxybenzene*, $C_{12}H_4ON_2Cl_4Br_2$, crystallises in characteristic groups of yellow needles and melts at 220—221°.

3 : 5-*Dichloro*-4-*bromoaniline*, $C_6H_4NCl_2Br$, crystallises in colourless needles, melts at 126°, and forms a sparingly soluble *sulphate*.

The reduction of 3 : 3′-dinitroazoxybenzene with stannous chloride and hydrochloric acid in alcoholic solution leads to the formation of 3 : 3′-diaminoazoxybenzene but not of *m*-nitroaniline. The primary

products in the reduction of nitro-compounds by ammonium sulphide cannot be hydroxylamines and nitroso-compounds, as whilst *m*-nitroaniline is formed from *m*-dinitrobenzene, no trace of it is obtained on treating with ammonium sulphide 3 : 3′-dinitroazoxybenzene, which is formed by reduction of *m*-dinitrobenzene with sodium sulphide.

Acetyl-s-*dinitroanilide*, $C_8H_7O_5N_3$, crystallises in needles and melts at 186—187°. s-*Nitrophenylenediamine*, $C_6H_7O_2N_3$, is formed by reduction of *s*-trinitrobenzene or of *s*-dinitroaniline with ammonium sulphide in boiling alcoholic solution; it is purple-red, melts at 140—141°, and forms a *diacetyl* derivative, $C_{10}H_{11}O_4N_3$, melting at 270°. G. Y.

Isomerism of the so-called Ethyl Benzeneazocyanoacetate. ARTHUR HANTZSCH and K. J. THOMPSON (*Ber.*, 1905, 38, 2266—2276. Compare Weissbach, Abstr., 1903, i, 541).—Weissbach's supposed stereoisomeric ethyl benzeneazocyanoacetates were the α- and β-modifications of ethyl phenylhydrazonecyanoacetate containing traces of formazyl cyanide, which is formed from diazonium salts and ethyl cyanoacetate in strongly alkaline solution.

When free from the α-modification, ethyl β-phenylhydrazonecyanoacetate melts at 85—86°.

That the two modifications of ethyl phenylhydrazonecyanoacetate are stereoisomeric is shown by the occurrence of one modification only of the following symmetrical hydrazones:

Ethyl phenylhydrazonemesoxalate, $NHPh\cdot N:C(CO_2Et)_2$, formed by the action of diazonium salts on ethyl malonate in presence of sodium acetate in aqueous-alcoholic solution, is an oil; it is hydrolysed by 1 mol. of alkali hydroxide at the laboratory temperature to ethyl hydrogen phenylhydrazonemesoxalate, melting at 114°.

Ethyl p-*bromophenylhydrazonemesoxalate* crystallises in yellow needles and melts at 76°.

Methyl phenylhydrazonemesoxalate (von Pechmann, Abstr., 1895, i, 329) is easily hydrolysed by aqueous alkali hydroxides; hydrolysis with 1 mol. of alkali hydroxide in ethyl alcoholic solution leads to the formation of a mixture of the monomethyl and monoethyl esters.

The phenylhydrazone of mesoxalonitrile crystallises with $\frac{1}{2}$ mol. of benzene and decomposes at 146—147° (compare Schmidtmann, Abstr., 1896, i, 458).

In its acidity and in its behaviour towards acetylising agents, ethyl α-phenylhydrazonecyanoacetate resembles the phenylhydrazone of mesoxalonitrile, whilst the β-modification resembles the esters of phenylhydrazonemesoxalic acid: to the α-modification, therefore, is to be ascribed the configuration $\begin{array}{l}CN\cdot C\cdot CO_2Et\\ NHPh\cdot N\end{array}$, and to the β-modification $\begin{array}{l}CN\cdot C\cdot CO_2Et\\ \quad N\cdot NHPh\end{array}$.

The protection of the carboxylic group by the proximity of the group –NHPh explains the formation of phenylhydrazonemesoxalic acid in hydrolysis of the β-form with sodium carbonate, whilst under the same conditions the α-form yields phenylhydrazoneglyoxylic acid. G. Y.

Azo-colouring Matters derived from *ar*-Tetrahydro-α-Naphthylamine. GILBERT T. MORGAN and F. E. RICHARDS (*J. Soc. Chem. Ind.*, 1905, **24** 652. Compare Trans., 1904, **85**, 736).—I. Azo- and Disazo-derivatives of *ar*-Tetrahydro-α-naphthylamine.—*ar*-Tetrahydro-α-naphthylamineazobenzenesulphonic acid dyes wool an orange shade from an acid-bath; its sodium salt crystallises in brownish-orange scales; after diazotising, it condenses with 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid to yield a disazo-compound of the formula $SO_3Na\cdot C_6H_4\cdot N_2\cdot C_{10}H_{10}\cdot N_2\cdot C_{10}H_3(OH)_2(SO_3Na)_2$, which when dyed on wool from an acid-bath gives reddish-violet shades; it condenses in the same way with "*R*-salt," and with α-naphthol-4-sulphonic acid, forming disazo dyes which give reddish-brown shades.

Naphthaleneazo-ar-*tetrahydro-α-naphthylamine*, $C_{10}H_7\cdot N_2\cdot C_{10}H_{10}\cdot NH_2$, obtained by condensing diazotised α-naphthylamine with *ar*-tetrahydro-α-naphthylamine, separates from methyl alcohol in reddish-black nodular crystals.

p-*Nitrobenzeneazo*-ar-*tetrahydro-α-naphthylamine*,

$$NO_2\cdot C_6H_4\cdot N_2\cdot C_{10}H_{10}\cdot NH_2,$$

is produced by adding an acetic acid solution of *p*-nitrobenzenediazonium chloride to an alcoholic solution of *ar*-tetrahydro-α-naphthylamine, and liberating the base from the hydrochloride so formed by ammonia; it crystallises from ethyl acetate in dark brown flakes.

Tetrahydro-α-naphthaleneazo-ar-*tetrahydro-α-naphthylamine*, obtained by condensing diazotised tetrahydro-α-naphthylamine with another molecular proportion of the base in acetic acid solution, crystallises from ethyl acetate in brownish-orange needles melting at 135—140°.

II. Substantive Polyazo-colouring Matters from *ar*-Tetrahydro-α-naphthylamine.

Ditolyldisazo-ar-*tetrahydro-α-naphthylamine*, $C_{14}H_{12}(N_2\cdot C_{10}H_{10}\cdot NH_2)_2$, is formed from *ar*-tetrahydro-α-naphthylamine (2 mols.) and tetrazotised tolidine. It dissolves in alcohol to an orange-brown solution; its hydrochloride is a black powder which dissolves in alcohol to a purple solution. This hydrochloride on diazotising combines with 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid and with α-naphthol-4-sulphonic acid to form black powders with metallic lustre which are sparingly soluble in cold water to a reddish-violet solution, and develop intense blue colorations with concentrated sulphuric acid. The former gives greyish-blue shades on unmordanted cotton, and the latter heliotrope tints.

The diazo-compound, obtained by condensing one molecule of the tetrahydro-base with tetrazotised tolidine, when again diazotised and coupled with 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid or with α-naphthol-4-sulphonic acid, gives rise to dyes which colour unmordanted cotton dark blue and reddish-heliotrope respectively.

III. Azo-derivatives of *ar*-Tetrahydro-α-naphthylamine-4-sulphonic Acid.

Most of the points dealt with under this head have been already published in Trans., 1904, **85**, 736.

IV. Azo-derivatives of Dimethyl-*ar*-tetrahydro-α-naphthylamine.

Dimethyl-ar-*tetrahydro-α-naphthylamine* was prepared by heating

ar-tetrahydro-α-naphthylamine hydrochloride with methyl alcohol at 170—180°.

p-*Nitrobenzeneazodimethyl*-ar-*tetrahydro-α-naphthylamine*,

$$NO_2\cdot C_6H_4\cdot N_2\cdot C_{10}H_{10}\cdot NMe_2,$$

produced by coupling the base with *p*-nitrobenzenediazonium chloride, crystallises from alcohol in well-defined, deep red acicular prisms melting at 150—152°.

Sodium dimethyl-ar-*tetrahydro-α-naphthylamineazobenzenesulphonate*, $NMe_2\cdot C_{10}H_{10}\cdot N_2\cdot C_6H_4\cdot SO_3Na$, prepared by coupling the base with diazobenzenesulphonic acid, separates from aqueous solution in yellow-brown flakes. It gives red shades on wool from an acid-bath.

Throughout the paper the colours produced by the various dyes are compared with those obtained from the corresponding naphthalene analogues, and as a result the following conclusions are arrived at:

(1) *ar*-Tetrahydro-α-naphthylamine resembles α-naphthylamine in yielding directly aminoazo-compounds from which polyazo-colouring matters may be obtained.

(2) The azo- and disazo-colouring matters derived from *ar*-tetrahydro-α-naphthylamine, its sulphonic acid and dimethyl derivative, resemble their analogues of the benzene series in tinctorial properties, but differ from those of the naphthalene series. P. H.

Normal Diazoxides as Primary Products of the Interaction of Nitrosobenzenes and Hydroxylamine. Arthur Hantzsch (*Ber.*, 1905, **38**, 2056—2062. Compare Abstr., 1903, i, 664; 1904, i, 201; Bamberger, Abstr., 1895, i, 459; 1900, i, 531).—A mixture of nitrosobenzene and α-naphthol in alcoholic solution was treated with a concentrated aqueous solution of hydroxylamine hydrochloride, then with a concentrated sodium carbonate solution, and diluted finally with water; immediate "coupling" took place, and the α-naphthol-dye was obtained in a yield of 56 per cent. of the theoretical. In a similar experiment with β-naphthol, a 53 per cent. yield of the dye was obtained. In a third, an aqueous solution of 1 mol. of hydroxylamine hydrochloride and 1 mol. of potassium hydroxide was added slowly to an alcoholic solution of 1 mol. of nitrosobenzene and excess of β-naphthol; a 48 per cent. yield of the dye was obtained, and no *anti*-diazoxide could be detected in the filtrate.

Contrary to Bamberger's statement, therefore, the primary product of the interaction of nitrosobenzene and hydroxylamine is the normal diazoxide. The failure to obtain more than traces of the dye under Bamberger's conditions is due to the instability of nitrosobenzene, as also of the normal diazoxides in alkali hydroxide solutions. Even on addition of a neutral solution of hydroxylamine hydrochloride and sodium hydroxide to a solution of nitrosobenzene at −10°, evolution of nitrogen ensues, and only traces of the dye are formed on subsequent addition of β naphthol.

Similar results are obtained with bromonitrosobenzene: in neutral solution at −10°, and with subsequent addition of β-naphthol, only traces of the dye; but in neutral solution, in presence of β-naphthol, 31 per cent., and in presence of β-naphthol and excess of sodium carbonate, 48 per cent., of the dye is obtained. At −5—0°, with

excess of potassium hydroxide, no trace of the dye, but *p*-dibromoazoxybenzene is obtained. These results are brought into agreement with the views of Angeli (Abstr., 1904, i, 699) if the action of hydroxylamine on nitrosobenzene is represented as resulting in the formation of the additive compound, which on elimination of water may yield either the normal diazoxide or the diazonium hydroxide:

$$\begin{array}{c} Ar\cdot N \\ \| \\ HO\cdot N \end{array} \longleftarrow \begin{array}{c} Ar\cdot N\cdot OH \\ | \\ HO\cdot N\cdot H \end{array} \longrightarrow \begin{array}{c} Ar\cdot N\cdot OH \\ \||| \\ N \end{array}.$$

G. Y.

Velocity of Decomposition of *p*-Nitrobenzenediazonium-chloride. Carl Schwalbe (*Ber.*, 1905, **38**, 2196—2199).—Cain and Nicoll's formula (Trans., 1902, **81**, 1412) for the decomposition of aromatic diazo-compounds does not hold when applied to technical products in which free nitrous acid and salts are generally present. Nitrous acid very materially hastens the rate of decomposition of diazo-compounds; salts, on the other hand, increase their stability. They are also much less stable in concentrated solution than in dilute.

E. F. A.

Action of Diazo-compounds on Primary Aliphatic Amines. Otto Dimroth (*Ber.*, 1905, **38**, 2328—2330).—Whilst molecular amounts of diazo-compounds and primary aromatic amines unite to form diazoamino-compounds, and bisdiazo-compounds are formed only rarely, it was found by Goldschmidt and Badl (Abstr., 1889, 774) that bisdiazo-compounds only were formed by the action of aromatic diazonium salts on methylamine, ethylamine, and allylamine.

Since the author has shown (this vol., i, 311) that fatty aromatic triazens are very labile, it appeared possible that the formation of these compounds had not been observed during the action of diazo-compounds on primary aliphatic amines owing to their instability.

It is now shown that the first phase of the action of a diazonium salt on a primary aliphatic amine consists in the formation of a triazen, which is readily distinguished from a bisdiazoamino-compound by the action of acids on it, when nitrogen is evolved in the cold.

The preparation of phenylmethyltriazen (compare Abstr., 1903, i, 450; and this vol., i, 311) from benzenediazonium chloride and methylamine is described, as also is the preparation of phenylethyltriazen (compare this vol., i, 311) from benzenediazonium chloride and ethylamine. A. McK.

Colour Reactions of Proteids with *p*-Dimethylaminobenzaldehyde and other Aromatic Aldehydes. Erwin Rohde (*Zeit. physiol. Chem.*, 1905, **44**, 161—170).—A pale-red coloration is obtained when a 2 per cent. solution of *p*-dimethylaminobenzaldehyde in normal hydrochloric acid is added to ordinary urine, and with certain pathological urines a deep-red coloration is produced. Proteids also yield similar colorations with the aldehyde in presence of concentrated acids. It is now shown that this coloration is due to the indole group

present in the proteids, and glutin which contains no indole nucleus gives no coloration. Hopkins and Cole's tryptophan, scatoleamino-acetic acid (Abstr., 1902, i, 193) or indoleaminopropionic acid (Ellinger, Abstr., 1904, i, 640), gives the same coloration with great readiness in the presence of concentrated hydrochloric acid, but not always in the presence of concentrated sulphuric acid.

Glycine, alanine, aspartic acid, serine, lysine, arginine, histidine, cystine, glucosamine, and aminovaleric acid do not give the coloration. The following proteids give the reaction: casein, edestin, protalbumose, ovalbumin, serum-albumin, and heteroalbumose. This latter also gives Adamkiewicz's reaction with glyoxylic acid, although Pick states the contrary. No coloration is given by glutine, protamine, iodoalbumin, or aldehydoalbumins, and these substances do not give the Adamkiewicz reaction.

The red coloration is formed at the expense of the aldehydo-group, and colorations are given by all aromatic aldehydes which have been examined, but not by open-chain aldehydes or furfuraldehyde.

J. J. S.

Diamino-acids in Casein and Gelatin. A Correction. ZDENKO H. SKRAUP (*Monatsh.*, 1905, 26, 683. Compare Abstr., 1904, i, 538, 594; this vol., i, 398).—It is now found that the products of the hydrolysis of casein and gelatin previously described as diaminoadipic and diaminoglutaric acids are *d*-alanine and a mixture of *d*-alanine and glycine respectively.

Commercial casein, purified by Hammarsten's method, gives the alanine glycine mixture, whilst caseins of other origin yield pure alanine. G. Y.

Oxidation of Gelatin and of Egg-albumin with Calcium Permanganate. JOHN SEEMANN (*Zeit. physiol. Chem.*, 1905, 44, 229—264. Compare Kutscher and Zickgraf, Abstr., 1903, i, 666; Kutscher and Schenck, Abstr., 1904, i, 955; this vol., i, 251; Otori, this vol., i, 104; von Furth, *ibid.*, 497).—The following substances have been detected among the products obtained by the oxidation of gelatin and of egg-albumin with hot 10 per cent. calcium permanganate solution, namely: formic, acetic, butyric, and probably propionic and valeric acids; benzoic acid and benzaldehyde; oxalic and succinic acids, but not glutaric acid; oxaluramide and probably oxaluric acid. The succinic acid is probably derived from an arginine group or from those groups which yield aspartic acid when the albumins are hydrolysed. The formation of oxaluramide is accounted for by the assumption of a condensation product of an amino fatty acid and arginine, $R\vdots CH(NH_2)\cdot CO\cdot NH\cdot C(NH)\vdots NH\cdot[CH_2]_3\cdot CH(NH_2)\cdot CO_2H$, which, when oxidised, is ruptured at the points indicated and yields $NH_2\cdot CO\cdot CO\cdot NH\cdot CO\cdot NH_2$. J. J. S.

Monoamino-acids of Edestin from Cotton Seeds and their Behaviour with Gastric Juice. EMIL ABDERHALDEN and OTTO ROSTOSKI (*Zeit. physiol. Chem.*, 1905, 44, 265—275. Compare Abstr., 1904, i, 211).—By hydrolytic agents and by the prolonged action of

gastric juice obtained by Pawloff's method on edestin, glycine, alanine, aminovaleric acid, leucine, pyrrolidine-2-carboxylic acid, phenylalanine, aspartic acid, glutamic acid, serine, tyrosine (in small quantities), and tryptophan were obtained. W. D. H.

Monoamino-acids from the Edestin of Sunflower Seeds. EMIL ABDERHALDEN and BÉLA REINBOLD (*Zeit. physiol. Chem.*, 1905, **44**, 284—293).—From its decomposition products this edestin resembles others. Its behaviour to pancreatic digestion is also described. W. D. H.

Composition of Gliadin from Wheat. EMIL ABDERHALDEN and FRANZ SAMUELY (*Zeit. physiol. Chem.*, 1905, **44**, 276—283).—By hydrolysis with acid, gliadin yielded glycine, alanine, aminovaleric acid, pyrrolidine-2-carboxylic acid, leucine, glutamic acid, aspartic acid, phenylalanine, serine, tyrosine, tryptophan, histidine, and arginine. Lysine was absent. Of these, glutamic acid is the most abundant (27 per cent.); the other substances enumerated make up about 22 per cent. W. D. H.

Further Researches on Protamines. ALBRECHT KOSSEL and HENRY D. DAKIN (*Zeit. physiol. Chem.*, 1905, **44**, 342—346).—The simplest proteids, the protamines, do not yield leucine, phenylaminopropionic acid, hydroxypyrrolidinecarboxylic acid, or cystine. Sturine, however, yields leucine, but aminovaleric acid and pyrrolidine-2-carboxylic acid were not found, although these are obtained from other protamines. Scombrine appears to be the simplest proteid of all, being a combination of arginine with pyrrolidine-2-carboxylic acid and alanine. W. D. H.

Nucleo-proteid of the Liver. IV. JULIUS WOHLGEMUTH (*Zeit. physiol. Chem.*, 1905, **44**, 530—539. Compare Abstr., 1903, ii, 440; 1905, i, 103).—The decomposition products of liver-nucleoproteid found were *l*-xylose, xanthine, hypoxanthine, guanine, adenine, histidine (?), arginine, lysine, tyrosine, leucine, glycine, alanine, pyrrolidine-2-carboxylic acid, glutamic acid, aspartic acid, phenylalanine, aminohydroxysuberic acid, and diaminohydroxysebacic acid. W. D. H.

Preparation of Nucleic Acid. HENRY B. SLADE (*Amer. J. Physiol.*, 1905, **13**, 464—465).—One hundred pounds of yeast are vigorously stirred with 1·1 per cent. of its weight of sodium hydroxide, dissolved in a little water and 2 or 3 times as much crystallised sodium acetate added. The mixture, after remaining at room-temperature for 24 hours, is boiled gently for an hour, and glacial acetic acid added until it is faintly acid. When cold, it is filtered and magnesium sulphate added to the filtrate to 5 per cent. strength, and then hydrochloric acid with constant stirring until a flocculent precipitate of nucleic acid forms. The presence of 2·5 per cent. of the acid usually effects a complete separation. The yield of nucleic acid is 0·5 per cent. of the yeast used; this contains 7 per cent. of phosphorus. If the method is

varied by boiling at once, the yield is less, and a nuclein compound which forms an insoluble copper compound is obtained. Under varying conditions, a series of cleavage products is formed, as Neumann found with thymo-nucleic acid. The simplest member of this series appears to be a thyminic acid. W. D. H.

[Oxidation of Nucleic Acids.] FRIEDRICH KUTSCHER (*Zeit. physiol. Chem.*, 1905, **44**, 317—319. Compare Abstr., 1904, i, 127, and Burian, *ibid.*, 358, 956).—A discussion of the relationships between nucleic acids, nuclein bases, and uric acid. J. J. S.

Oxidation of Thymonucleic Acid with Calcium Permanganate. FRIEDRICH KUTSCHER and MARTIN SCHENCK (*Zeit. physiol. Chem.*, 1905, **44**, 309—316. Compare Kutscher and Seemann, Abstr., 1904, i, 127).—The following products have been obtained by oxidising thymonucleic acid in the form of its soluble acid barium salt with 10 per cent. calcium permanganate solution at a temperature of nearly 100° :—Oxalic, martamic, and acetic acids, adenine, guanidine, and carbamide. *Martamic acid*, $C_5H_8O_5N_6$ or $C_5H_{10}O_5N_6$, may be separated from the oxalic acid by means of its *calcium* salt; this is moderately soluble in water, from which it crystallises in fine needles. The acid crystallises in slender, microscopic needles, and does not give either the murexide or Weidel reaction. It is sparingly soluble in cold water or ether, and when heated in a melting-point tube sublimes without melting or decomposing.

Small amounts of another acid and of a biuret derivative were also isolated. J. J. S.

Protagon. N. ALBERTO BARBIERI (*Compt. rend.*, 1905, **140**, 1551—1553).—Another contribution to the much-debated question whether protagon is a chemical individual. The view taken is that protagon is non-existent in the cerebral tissues, but is a mixture of cerebrin and the substance first described by Fremy as cerebric acid. W. D. H.

Cerebron. HANS THIERFELDER (*Zeit. physiol. Chem.*, 1905, **44**, 366—370).—The formula given to cerebron is $C_{48}H_{93}O_9N$. On hydrolysis, it is resolved, as shown in the following equation, into cerebronic acid, sphingosin, and galactose: $C_{48}H_{93}O_9N + 2H_2O = C_{25}H_{50}O_3 + C_{17}H_{35}O_2N + C_6H_{12}O_6$. W. D. H.

Spectroscopy of Blood and of Oxyhæmoglobin. II. A. VILA and M. PIETTRE (*Bull. Soc. chim.*, 1905, [iii], **33**, 573—580. Compare this vol., ii, 500; Bohr, Abstr., 1890, 450).—The authors have investigated the influence of various substances on the absorption spectra of solutions of blood and of oxyhæmoglobin in water. Dilute sodium chloride solution suppresses the band λ 634 in the red, a concentrated solution produces a new band, λ 597, sodium fluoride displaces the band λ 634 to a position λ 612, even in presence of other salts (compare

Menzies, Abstr., 1895, i, 256, and Ville and Derrien, this vol., i, 500), except in the case of sodium nitrite, when the displacement is to the position λ 620. The band in the red is intensified by the addition of oxidising or reducing agents; this effect is similar to that induced by drying or aging of blood or oxyhæmoglobin. The authors conclude that the colouring matter present in living blood corpuscles shows two absorption bands in the green and that it undergoes change the moment it escapes from the corpuscle and then shows the additional band λ 634 in the red, which also characterises oxyhæmoglobin. This absorption band in the red must be associated with a very stable nucleus, since it is also shown by solutions of the brown oil produced by fusing oxyhæmoglobin with potassium hydroxide.

These observations also show that oxyhæmoglobin and methæmoglobin are identical, as has already been indicated by Otto and Hüper's analyses of the two substances. T. A. H.

Methæmoglobin. M. Piettre and A. Vila (*Compt. rend.*, 1905, **140**, 1350—1352. Compare this vol., i, 500; ii, 402).—Polemical against Ville and Derrien, who attribute the new band described by the authors to admixture with methæmoglobin. W. D. H.

Methæmoglobin and its Fluorine Compound. Jules Ville and Eugène Derrien (*Compt. rend.*, 1905, **140**, 1549—1551. Compare this vol., i, 500; ii, 402, and preceding abstract).—Polemical against Piettre and Vila. The view that the new absorption band is due to methæmoglobin is emphasised. The statement made by Piettre and Vila that their material cannot be methæmoglobin because it is crystallisable is shown to be incorrect. Numerous observers in the past have obtained methæmoglobin in crystalline form. W. D. H.

Carboxyhæmochromogen. Fritz Pregl (*Zeit. physiol. Chem.*, 1905, **44**, 173—181).—The statement originally made by Hoppe-Seyler, that the proportion of carbon monoxide in carboxyhæmochromogen is 1 mol. of the gas per atom of iron, is confirmed. It is also found that 5 atoms of nitrogen are present per atom of iron. Much of the present paper is devoted to the method of preparation of the hæmochromogen and the prevention of its conversion into hæmatin by the air. W. D. H.

Hæmatin. William Küster (*Zeit. physiol. Chem.*, 1905, **44**, 391—421. Compare Abstr., 1896, i, 516; 1900, i, 68, 319; 1901, i, 58, 298; 1902, i, 845).—The product, insoluble in water, which is obtained by oxidising hæmatin with chromium trioxide in acetic acid solution (Abstr., 1900, i, 69) has been further investigated. The best yield (40 per cent.) is obtained when 12 atoms of oxygen are used for each molecule of hæmatin. When treated with 25 per cent. sulphuric acid or with concentrated hydrochloric acid, chromic salts and hæmatic and oxalic acids are removed and the amount of iron is considerably reduced. Some of the properties of this purified product have been examined. On further oxidation with chromium trioxide, it yields

tribasic hæmatic acid, and with nitric acid it yields oxalic, succinic, and tribasic hæmatic acid.

In the oxidation of hæmin with nitric acid, the yield of oxalic acid is greater the more concentrated the acid. The other products isolated were succinic and hæmatic acids.

Hæmatin has been oxidised with hydrogen peroxide, with sodium hypobromite, with calcium permanganate in alkaline solution, and with chromic acid in acetic acid solution, but no new products have been isolated.

Hæmatoporphyrin, when oxidised with chromic acid in sulphuric acid solution, yields the same acids, namely, oxalic, succinic, and hæmatic. In the purification of hæmatic acid as its calcium salt, a new acid has been isolated. It crystallises from hot water, contains nitrogen, does not melt at 240°, yields a readily soluble calcium salt, and gives the pyrrole reaction. J. J. S.

Absorption of Ferments by Colloids. FERDINAND DAUWE (*Beitr. chem. Physiol. Path.*, 1905, **6**, 426—453).—A discussion with some experiments on the question whether absorption or adsorption will best explain the diminution in the amount of ferment which occurs when colloids are present. Whether the union is purely physical, or whether a loose chemical compound is formed, is a question to which no clear answer is given, although it appears improbable that such different materials as coagulated proteid, animal charcoal, kieselguhr, &c., which act in the same way, form definite compounds either with ferments or colouring matters. W. D. H.

Catalase. ALEXIS BACH (*Ber.*, 1905, **38**, 1878—1885. Compare Abstr., 1903, i, 671; 1904, i, 792).—The amount of hydrogen peroxide decomposed by animal catalase is found to depend both on the concentration of the peroxide and on that of the ferment. When the catalase present has reached a maximum, the amount changed is directly proportional to the quantity of hydrogen peroxide present, whilst when the hydrogen peroxide has reached a maximum, the change is directly proportional to the concentration of the ferment. The time taken by varying amounts of catalase to hydrolyse a given quantity of hydrogen peroxide decreases very much more rapidly than the quantity of ferment increases.

An attempt to compare by means of pyrogallol the distribution of hydrogen peroxide between peroxydase and catalase when both ferments are present failed, since, although the presence of catalase had no effect on the oxidation of pyrogallol by the peroxydase-hydrogen peroxide system, the pyrogallol acted injuriously on the catalase and prevented any liberation of oxygen. It is, however, also possible that, if the velocity of formation of the peroxydase-hydrogen peroxide complex is large, the peroxide will be completely withdrawn from the influence of the catalase. E. F. A.

Mode of Action of Philocatalase. F. BATTELLI and Mlle. L. STERN (*Compt. rend.*, 1905, **140**, 1352—1353. Compare this vol.,

ii, 406).—Philocatalase protects catalase in a two-fold manner, namely, by a destruction of anticatalase and a regeneration of catalase.

W. D. H.

Saccharification of Artificial Starches by Malt. Eugène Roux (*Compt. rend.*, 1905, **140**, 1259—1261).—The action of malt diastase on various artificial starches (this vol., i, 262, 328) is found to be very similar to the action on flour starch. Maltose and dextrins are formed, the relative proportions of which depend on the temperature at which the action takes place. Under the same conditions, about 20 per cent. more maltose is produced from the artificial starches as compared with flour starch. The dextrins are almost completely soluble in alcohol.

H. M. D.

Influence of Liquefaction of Starch on its Transformation by Saccharifying Diastases. Auguste Fernbach and Jules Wolff (*Compt. rend.*, 1905, **140**, 1067—1069).—The effect of the liquefying action of malt extract is similar to that of heat under pressure. In both cases, a considerable amount of starch remains untransformed after treatment with barley extract.

N. H. J. M.

Organic Chemistry.

Trimethylene-trisulphone and -disulphonesulphide. WALTER PETERS (*Ber.*, 1905, **38**, 2565—2567. Compare Camps, Abstr., 1892, 591, 592).—The dibromide and hexabromide of trimethylenetrisulphone are represented respectively by the formulæ $SBr_2{<}{CH_2 \cdot SO_2 \atop CH_2 \cdot SO_2}{>}CH_2$ and $SBr_2{<}{CBr_2 \cdot SO_2 \atop CH_2 - SO_2}{>}CBr_2$, as in both compounds two bromine atoms are very loosely combined. For example, the bromine atoms are removed by ammonia, by silver nitrate solution, or by sodium hydroxide in the form of hypobromite, and the compounds readily liberate iodine from a hot solution of potassium iodide.

The sodium salt of the trimethylenetrisulphone is hydrolysed to a considerable extent in aqueous solution, as shown by alkalimetric methods. J. J. S.

Aqueous Solutions of Acetylcarbinol. ANDRÉ KLING (*Bull. Soc. chim.*, 1905, [iii], **33**, 755—760).—It has already been shown (Abstr., 1903, i, 138, 223) that in aqueous solution acetylcarbinol reacts to a certain extent as the tautomeric oxide, $OH \cdot CMe{<}{CH_2 \atop O}{|}$. In the anhydrous state, however, it reacts as a ketone. Thus (*a*) its reaction with Grignard's reagents is perfectly normal (Abstr., 1904, i, 2, 133). (*b*) Its molecular magnetic rotation is 3·650, and that calculated for the ketonic formula is 3·659 (Perkin, Proc., 1891, 790). (*c*) Its molecular refraction is 17·643, corresponding with 17·614 for the ketonic formula, whereas the oxide formula requires 17·016.

The tautomerising action of the water is attributed to the intermediate formation of hydrates; for example,

$$CH_3 \cdot CO \cdot CH_2 \cdot OH \longrightarrow CH_3 \cdot C(OH)_2 \cdot CH_2 \cdot OH \longrightarrow OH \cdot CMe{<}{CH_2 \atop O}{|}.$$

An examination of the viscosities of aqueous solutions of acetylcarbinol by Varenne and Godefroy's method (Abstr., 1904, i, 2; ii, 160) indicates the formation of hydrates with H_2O, $2H_2O$, $4H_2O$, and $11H_2O$. Aqueous solutions of acetylcarbinol have a faintly acid reaction, and are only slowly neutralised by alkalis; thus the first few drops of alkali render the solution neutral, but after some time the solution again becomes feebly acid, and the process can be repeated several times in the cold before permanent neutralisation is attained. Acetylcarbinol is thus a pseudo-acid, and this conclusion has been confirmed by an examination of the electrical conductivities of solutions of acetylcarbinol in presence of sodium hydroxide. J. J. S.

Preparation of Thio-acids and Disulpho-acids. EINAR BIILMANN (*Annalen*, 1905, **339**, 351—372).—The non-crystalline thio-acids, which seem so far not to have been prepared in a pure state,

can be obtained by treating alkali salts of halogen-substituted fatty acids with potassium xanthate in aqueous solution, thus: $OEt{\cdot}CS_2K + CH_2Cl{\cdot}CO_2K = OEt{\cdot}CS{\cdot}S{\cdot}CH_2{\cdot}CO_2K + KCl$. On further treatment with ammonia, the xanthamides are formed, thus:

$$OEt{\cdot}CS{\cdot}S{\cdot}CH_2{\cdot}CO_2H + 2NH_3 = OEt{\cdot}CS{\cdot}NH_2 + SH{\cdot}CH_2{\cdot}CO_2{\cdot}NH_4.$$

Xanthylacetic acid, $C_5H_8O_3S_2$, is prepared from potassium xanthate and sodium chloroacetate in aqueous solution; the mixture is kept overnight; since the xanthylacetic acid on heating in alkaline solution condenses to trithiocarbonylacetic acid, $CS(S{\cdot}CH_2{\cdot}CO_2H)_2$, it is necessary to cool with ice when preparing large quantities. The acid, which is a white, crystalline, odourless solid melting at 53—54°, forms hygroscopic alkali salts; the *lead* salt, $(C_5H_7O_3S_2)_2Pb,H_2O$, is a microcrystalline precipitate. On evaporating an alcoholic solution of the acid with ammonia, xanthamide is formed; the latter is converted by treatment with hydrogen chloride into thioglycollic acid, which is a colourless oil boiling at 123° under 29 mm. pressure; it forms an insoluble *barium* salt. *Disulphideacetic acid*, $S_2(CH_2{\cdot}CO_2H)_2$, prepared by oxidation of crude thioglycollic acid by means of iodine, melts at 107—108° and gives a precipitate of silver sulphide with ammoniacal silver solution.

α-Xanthylpropionic acid, $OEt{\cdot}CS{\cdot}S{\cdot}CHMe{\cdot}CO_2H$, prepared from sodium α-bromopropionate and potassium xanthate, is a colourless, crystalline substance melting at 49—50°; the alkali salts are hygroscopic, and the lead salt is unstable. *α-Disulphidepropionic acid*, $S_2(CHMe{\cdot}CO_2H)_2$, forms white crystals melting at 140—142°. *β-Xanthylpropionic acid*, prepared from β-iodopropionic acid, forms crystals melting at 66°; the *sodium* salt crystallises with $3H_2O$ in white, rectangular leaflets. β-Disulphidepropionic acid crystallises in white leaflets melting at 155°, and does not blacken with ammoniacal silver solution.

α-Xanthylbutyric acid, prepared from sodium α-bromobutyrate and potassium xanthate, forms white crystals melting at 55°. *α-Thiolbutyric acid*, $SH{\cdot}CHEt{\cdot}CO_2H$, is an oil boiling at 118—122° under 19 mm. pressure; its basic *lead* salt is insoluble.

Xanthylsuccinic acid, $OEt{\cdot}CS{\cdot}S{\cdot}CH{\cdot}(CO_2H){\cdot}CH_2{\cdot}CO_2H$, prepared from sodium bromosuccinate, crystallises in plates melting at 149°. Thiomalic acid forms crystals melting at 148°, and gives a characteristic reaction with copper sulphate.

Attempts to prepare thiotartaric acid lead to no result; potassium xanthate and dibromosuccinic acid give fumaric acid and *ethyl dioxyperthiocarbonate*, $\begin{matrix} S{\cdot}CS{\cdot}OEt \\ | \\ S{\cdot}CS{\cdot}OEt \end{matrix}$.

K. J. P. O.

α-Alkylacrylic Acids. EDMOND E. BLAISE and A. LUTTRINGER (*Bull. Soc. chim.*, 1905, [iii], 33, 760—783. Compare this vol., i, 168).—The esters of α-alkylacrylic acids have been prepared by the action of phosphoric oxide on the esters of the corresponding hydracrylic acids (this vol., i, 505). *Ethyl α-ethylacrylate*, $CH_2{:}CEt{\cdot}CO_2Et$, is obtained together with *α-ethylacrylic acid*, tiglic acid, and the *ester*, $CH_2{:}CEt{\cdot}CO_2{\cdot}CH_2{\cdot}CHEt{\cdot}CO_2Et$ (derived from α-ethylacrylic acid and α-ethylhydracrylic acid), by the action of phosphoric oxide on a benzene

solution of ethyl α-hydracrylate. The complex ester boils at 144—146° under 24 mm. pressure, and when hydrolysed yields the two components, which were recognised by means of their reactions with phenylhydrazine at 140°. Ethyl α-ethylacrylate is a liquid distilling at 137° under atmospheric pressure, and the yield is some 65 per cent. The acid distils at 83° under 15 mm. pressure, melts at −16°, and dissolves only sparingly in water, but readily in organic solvents. The *potassium hydrogen* salt, $KH(C_5H_7O_2)_2$, and *ammonium* salt are both readily soluble in water. The *chloride*, $CH_2{:}CEt{\cdot}COCl$, distils at 25° under 13 mm., or at 38·5° under 30 mm. pressure. The *amide* melts at 83·5°, the *anilide* at 82°, the *phenylhydrazide*, $CH_2{:}CEt{\cdot}CO{\cdot}NH{\cdot}NHPh$, at 77°, and the *dibromide*, *αβ-dibromo-α-ethylpropionic acid*, obtained by the addition of bromine in carbon disulphide solution at 0°, crystallises from light petroleum and melts at 73°. *β-Bromo-α-ethylpropionic acid*, obtained by the addition of hydrogen bromide to the unsaturated acid, distils at 128—129° under 15 mm. pressure, and its *ethyl* ester at 94—95° under 20 mm. pressure. The corresponding *iodo*-acid, $CH_2I{\cdot}CHEt{\cdot}CO_2H$, crystallises from light petroleum, melts at 28°, and is extremely hygroscopic.

Ethyl α-ethylacrylate condenses with ethyl acetoacetate in the presence of sodium ethoxide at the ordinary temperature, yielding *ethyl α′-acetyl-α-ethylglutarate*, $CO_2Et{\cdot}CHAc{\cdot}CH_2{\cdot}CHEt{\cdot}CO_2Et$, which distils at 150° under 10 mm. pressure, and ethyl α-ethylglutarate (Auwers and Titherley, Abstr., 1896, i, 639). This latter is the only product when the condensation is effected by heating the mixture for six hours on the water-bath. When boiled with hydrochloric acid, the acetylethylglutarate is hydrolysed yielding carbon dioxide, ethyl alcohol, and *γ-acetyl-α-ethylbutyric acid*, $CH_2Ac{\cdot}CH_2{\cdot}CHEt{\cdot}CO_2H$, which distils at 158° under 9 mm. pressure. The *semicarbazone* of the acid forms small crystals from a mixture of absolute ether and alcohol and melts at 125°.

Aniline reacts with α-ethylacrylic acid at its boiling point, yielding the anilide of the acid together with *β-phenylamino-α-ethylpropionanilide*, $NHPh{\cdot}CH_2{\cdot}CHEt{\cdot}CO{\cdot}NHPh$, which crystallises in slender needles melting at 115° (compare Autenrieth and Pretzell, Abstr., 1903, i, 474).

α-Ethylacrylic acid condenses with phenylhydrazine, yielding 1-*phenyl*-4-*ethyl*-5-*pyrazolidone*, $NPh<\begin{matrix}CO-CHEt\\ NH\cdot CH_2\end{matrix}$, which melts at 79° and distils at 213—214° under 15 mm. pressure. Its 2-*acetyl* derivative, $NPh<\begin{matrix}CO-CHEt\\ NAc\cdot CH_2\end{matrix}$, melts at 54—55° and distils at 213—214° under 28 mm. pressure. When heated with methyl iodide for six hours at 120°, the pyrazolidone yields the *compound*, $NPh<\begin{matrix}CO-\!\!\!-\!\!\!-CHEt\\ NHMeI\cdot CH_2\end{matrix}, I_2$, melting at 126°, and when oxidised with potassium ferricyanide it yields 1-*phenyl*-4-*ethyl*-5-*pyrazolone*,

$$NPh<\begin{matrix}CO\cdot CHEt\\ N=CH\end{matrix},$$

melting at 78°. α-Ethylacrylic acid and hydrazine hydrate react

yielding, among other products, a substance melting at 100°, distilling at about 300°, and containing 15·86 per cent. of nitrogen.

Ethyl a-propylacrylate (52 per cent. yield) distils at 156° under atmospheric pressure. The *acid* melts at −17° and distils at 101—102° under 15 mm. pressure. The *potassium* salt,

$$CH_2\colon CPr\cdot CO_2K,$$

crystallises from alcohol in brilliant plates. The acid, when boiled with aniline, yields *β-phenylamino-a-propylpropionanilide*,

$$NHPh\cdot CH_2\cdot CHPr\cdot CO\cdot NHPh,$$

melting at 118·5° and soluble in hydrochloric acid.

*Ethyl a-*iso*propylacrylate* distils at 153° under the ordinary pressure, the *acid* at 100° under 19 mm. pressure, and its *dibromide*, *aβ-dibromo-a-*iso*propylpropionic* [*a-bromo-β-methyl-a-bromomethylbutyric*] *acid*,

$$CHMe_2\cdot CBr(CH_2Br)\cdot CO_2H,$$

melts at 87°. *Ethyl a-butylacrylate* distils at 177°, the *acid* boils at 109—110° under 10 mm. pressure, and solidifies at −15°. The *potassium hydrogen*, *ammonium*, and *calcium* salts are all anhydrous, and the *cupric* salt crystallises with $5H_2O$. The *acid chloride* distils at 58—59° under 13 mm. pressure. The *anilide* melts at 41·5°, and the *phenylhydrazide* at 91·5°. The acid combines with hydrogen bromide, yielding *β-bromo-a-butylpropionic* [*a-bromomethylhexoic*] *acid*, which is an oil; its *ethyl* ester distils at 120—121° under 18 mm. pressure. 1-*Phenyl*-4-*butyl*-5-*pyrazolidone* melts at 84°.

Ethyl a-butylacrylate and ethyl cyanoacetate condense in presence of sodium ethoxide yielding *ethyl γ-cyano-a-butylglutarate*,

$$CO_2Et\cdot CH(C_4H_9)\cdot CH_2\cdot CH(CN)\cdot CO_2Et,$$

which distils at 192° under 20 mm. pressure. When hydrolysed, the ester yields *heptane-aaγ-tricarboxylic acid*,

$$CH_3\cdot[CH_2]_3\cdot CH(CO_2H)\cdot CH_2\cdot CH(CO_2H)_2,$$

which melts at 144°.

Ethyl a-heptylacrylate distils at 122° under 18 mm. pressure and the *acid* at 158° under the same pressure. The *potassium* salt crystallises from alcohol in plates. J. J. S.

Preparation of Dimethylacrylic Acid. PHILIPPE BARBIER and GEORGES LÉSER (*Bull. Soc. chim.*, 1905, [iii], 33, 815—816).—The acid is readily prepared by adding pure mesityl oxide to a well-stirred solution of sodium hypochlorite, prepared by Graebe's method; the mixture becomes hot, and, when it has again attained the ordinary temperature, the excess of hypochlorite is destroyed by sodium hydrogen sulphite. The solution is decanted from the chloroform and acidified with sulphuric acid, when crystals of dimethylacrylic acid separate. A further quantity may be obtained by extracting the acid filtrate with ether. The yield is over 70 per cent. J. J. S.

Crotonic and *iso*Crotonic Acids. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1905, 254—255).—Crotonic and *iso*crotonic acids dissolved in glycerol were boiled for some time; in neither case was any gas evolved; the investigation is being continued. P. H.

The Five Isomeric Acids, $C_4H_6O_2$. WILLHELM AUTENRIETH (*Ber.*, 1905, **38**, 2534—2551).—The five acids of the formula $C_4H_6O_2$, $\begin{matrix} H\cdot C\cdot Me \\ \parallel \\ H\cdot C\cdot CO_2H \end{matrix}$, $\begin{matrix} Me\cdot C\cdot H \\ \parallel \\ H\cdot C\cdot CO_2H \end{matrix}$, $CH_2{:}CMe\cdot CO_2H$, $CH_2{:}CH\cdot CH_2\cdot CO_2H$, and $CH_2{<}\begin{matrix} CH_2 \\ | \\ CH\cdot CO_2H \end{matrix}$, are now known as uniform individuals. That four of these acids contain an ethylenic linking is shown by the fact that the anilides obtained from them unite with two atoms of bromine or one molecule of aniline to form saturated compounds. The fifth acid, trimethylenecarboxylic acid, is saturated, its anilide yielding a monobromo-substitution product.

β-Chlorocrotonic and β-chloro*iso*crotonic acids are $\alpha\beta$-unsaturated acids and are structurally identical, just as are crotonic and *iso*crotonic acids. The mercaptol esters of ethyl acetoacetate of the general type $CMe(SR)_2\cdot CH_2\cdot CO_2Et$, and the disulphonyl esters of the type $CMe(SO_2R)_2\cdot CH_2\cdot CO_2Et$, give, with alkalis, derivatives of *iso*crotonic acid. Further, with phenylhydrazine, ethyl β-chloro*iso*crotonate forms phenylmethylpyrazolone and other pyrazolone derivatives, containing a methyl group.

Since the tribromide, obtained by the action of bromine on *iso*crotonanilide, yields α-bromocrotonic acid only on hydrolytic decomposition by hydrochloric acid, the constitution of *iso*crotonic acid is regarded as definitely settled.

[With CARL PRETZELL.]—iso*Crotonanilide*, $\begin{matrix} Me\cdot C\cdot H \\ \parallel \\ H\cdot C\cdot CO\cdot NHPh \end{matrix}$, prepared by the action of aniline on *iso*crotonic chloride, crystallises in prisms and melts at 102°.

iso-*$\alpha\beta$-Dibromobutyryl*-p-*bromoanilide*,

$$\begin{matrix} Me\cdot CH\cdot Br \\ | \\ H\cdot CBr\cdot CO\cdot NH\cdot C_6H_4Br(1:4) \end{matrix},$$

prepared by the action of a solution of bromine in chloroform on *iso*crotonanilide, forms glistening prisms and melts at 146°. When heated with fuming hydrochloric acid at 120—130° for six hours, it forms α-bromocrotonic acid, melting at 106°, and *p*-bromoaniline.

Benzoyl-p-*bromoanilide*, prepared from *p*-bromoaniline by the Schotten-Baumann method, separates from alcohol in glistening, hexagonal plates and melts at 202°.

$\alpha\beta$-Dibromobutyryl-p-*bromoanilide*, $\begin{matrix} H\cdot CBrMe \\ | \\ H\cdot CBr\cdot CO\cdot NH\cdot C_6H_4Br \end{matrix}$, prepared by the action of bromine (2 atoms) on $\alpha\beta$-dibromobutyranilide or by the action of bromine (4 atoms) on crotonanilide, both reactions having been conducted in chloroform solution, separates from alcohol in glistening leaflets and melts at 154—155°. By its hydrolytic decomposition with hydrochloric acid at 130°, *p*-bromoaniline, hydrobromic acid, and a bromocrotonic acid (m. p. 97°) were obtained, the latter being probably identical with the acid designated in the literature as β-bromocrotonic acid.

Vinylacetanilide, $CH_2{:}CH\cdot CH_2\cdot CO\cdot NHPh$, separates from dilute alcohol in needles and melts at 58°. Its *dibromide*,

$$CH_2Br\cdot CHBr\cdot CH_2\cdot CO\cdot NHPh,$$

prepared by the action of bromine on a solution of the anilide in chloroform, crystallises in needles and melts at 101°.

Methylacrylanilide dibromide, $CH_2Br\cdot CBrMe\cdot CO\cdot NHPh$, prepared by the action of bromine on a chloroform solution of methylacrylanilide, separates from alcohol in needles and melts at 128°.

Trimethylenecarboxylic anilide, $CH_2<\begin{matrix}CH_2\\ |\\ CH\cdot CO\cdot NHPh\end{matrix}$, prepared by the addition of aniline to trimethylenecarboxylic chloride, separates from water or dilute alcohol in glistening leaflets and melts at 110—111°.

Trimethylenecarboxylic p-*bromoanilide*,

$$CH_2<\begin{matrix}CH_2\\ |\\ CH\cdot CO\cdot NH\cdot C_6H_4Br\end{matrix},$$

prepared by the bromination of the preceding compound, separates from alcohol in glistening prisms and melts at 189—190°.

Its constitution was determined by its behaviour on hydrolysis with fuming hydrochloric acid at 120°, when *p*-bromoaniline and an acid which did not contain bromine (probably trimethylenecarboxylic acid) were obtained. A. McK.

d-**Lactide.** Émile Jungfleisch and Marcel Godchot (*Compt. rend.*, 1905, **141**, 111—113. Compare Wislicenus, Abstr., 1873, 57).—If small quantities of *d*-lactic acid are heated at about 70° under 25 mm. pressure to complete elimination of water, and the product rapidly distilled at 150—155°, the distillate contains *d*-lactide only; but if large quantities of acid are distilled, the heating must be prolonged and the distillate contains *d*- and *i*-lactides, which can be separated by fractional crystallisation.

i-Lactide forms triclinic crystals, whilst those of the *d*-modification are orthorhombic. *d*-Lactide melts at 95°, distils at 150° under 25 mm. pressure, is highly hygroscopic, and is more soluble than the *i*-modification in ether, alcohol, chloroform, or benzene. The value of $[\alpha]_D$ for *d*-lactic acid decreases with dilution; solutions containing 1·1665, 0·5832, and 0·2916 gram of $C_6H_8O_4$ per 100 c.c. of benzene have $[\alpha]_D$ $-298°$, $-280°$, and $-246°$ respectively at 18°. In contact with water, *d*-lactide dissolves more rapidly than does the *i*-modification, the solution becoming acid and less lævorotatory owing to formation of *d*-lactyl-lactic acid, which is gradually partially hydrolysed into *d*-lactic acid, with which it forms an equilibrium in aqueous solution. Thus a solution of 0·117 gram of *d*-lactide in 30 c.c. of water immediately after formation and after 2, 6, 12, 48, and 72 hours has $[\alpha]_D$ $-192·8°$, $-141°$, $-111°$, $-59·8°$, $-42·7°$, and $-8°$ respectively at 13°. Similar changes take place, but more rapidly, at 100°. A concentrated solution of lævorotatory zinc *d*-lactyl-lactate is obtained by neutralising the freshly prepared aqueous solution of *d*-lactide with zinc carbonate and evaporating at low temperatures; this unstable salt could not be obtained in the crystalline state, as after some time in the cold, or more rapidly on boiling, the solution deposits zinc *d*-lactate, which is only slightly lævorotatory, and becomes acid owing to the formation of free *d*-lactic acid. Thus a solution of zinc *d*-lactyl-

lactate which had $[\alpha]_D$ $-7{\cdot}5°$, after some hours of boiling had $[\alpha]_D$ $-0{\cdot}3°$. G. Y.

ββ-Dimethylbutyrolactone. GUSTAVE BLANC (*Compt. rend.*, 1905, **141**, 203—204).—Blaise's supposed ββ-dimethylbutyrolactone (Abstr., 1898, i, 561) must be a mixture of that substance with the αα-dimethyl-compound, as the ethyl γ-bromodimethylbutyrate obtained from it boils at 102—104° under 9 mm. pressure, and when treated with ethyl sodiocyanoacetate yields only a small amount of ethyl cyano-αα-dimethyladipate, which boils at 175° under 8 mm. pressure and on hydrolysis is converted into αα-dimethyladipic acid melting at 87°, whilst the action of ethyl sodiocyanoacetate on the α-bromo-ester from ββ-dimethylbutyrolactone leads to the elimination of hydrogen bromide and the formation of the *ester*, $C_5H_9{\cdot}CO_2Et$. G. Y.

Ethyl Dicyanosuccinate. P. ENGLER and JULIUS MEYER (*Ber.*, 1905, **38**, 2486—2488).—When shaken with iodine in ethereal solution, ethyl sodiocyanoacetate yields *ethyl dicyanosuccinate*, $C_{10}H_{12}O_4N_2$, which crystallises in white leaflets, melts at 118°, and is insoluble and comparatively stable in cold water, but is easily hydrolysed by boiling water or aqueous alkali hydroxides, carbonates, or thiosulphates. The product of hydrolysis is probably diethyl dihydrogen ethanetetracarboxylate; the silver salt could not be obtained in a state of purity.

The action of iodine on a mixture of ethyl sodiomalonate and ethyl sodiocyanoacetate leads chiefly to the formation of ethyl ethanetetracarboxylate. G. Y.

Derivatives of Dibromo- and Dichloro-maleic Acid and their Conversion into Indigo. ALFRED SALMONY and HUGO SIMONIS (*Ber.*, 1905, **38**, 2580—2601. Compare Abstr., 1901, i, 268).—Good yields of dibromo- and dichloro-maleic acids may be obtained by oxidising mucobromic and mucochloric acids (Abstr., 1899, i, 741) by Hendrixon's method (Abstr., 1890, 958).

The following salts of dibromomaleic acid have been prepared: *potassium* ($1H_2O$), *sodium potassium*, *cobalt* ($2H_2O$).

Ethyl hydrogen dibromomaleate, obtained by the half esterification of the acid, forms a solid mass melting at 100° and decomposing into the anhydride and alcohol when heated. The *propyl hydrogen* ester and the *amyl hydrogen* ester are oils, and their stability increases with the complexity of the alkyl group present. The normal methyl ester (Abstr., 1888, 1058) is best obtained by the hydrogen chloride catalytic method. The normal *allyl* ester and the corresponding tert.-*butyl* ester are oils. The iso*amyl* ester distils at 320°. In the preparation of the esters from the silver salts and alkyl iodides, it is essential that no free iodine should be present, as this readily transforms the maleates into the corresponding fumarates.

The following salts and esters of dichloromaleic acid have been prepared: *potassium* (H_2O), *sodium* (H_2O), *sodium hydrogen* (H_2O), *lithium*, *cupric* (H_2O), *plumbous* (H_2O), *nickelous* ($2H_2O$). The iso*butyl hydrogen* ester distils at 168—170°, but is partially decomposed. *Aniline dibromomaleate*, $C_2Br_2(CO_2NH_3Ph)_2$, obtained when cold alcoholic solutions of the components are mixed, crystallises in soft, glistening, white scales. It begins to decompose at 128°, dissolves

readily in water, and only sparingly in most organic solvents with the exception of carbon disulphide. The *o-toluidine* salt crystallises in needles melting at 139°, and the *p-compound* in plates decomposing at 154°. *Aniline dichloromaleate* begins to decompose at 125°.

When aniline and the dibromo-acid are boiled with water and a little ether and the solution subsequently evaporated, a mixture of two isomeric *anilinobromomaleic anhydride anils* is obtained. The one, $\begin{matrix}NHPh\cdot C\cdot C(NPh) \\ CBr—CO\end{matrix}\!\!>\!O$, crystallises from 90 per cent. alcohol in yellowish-green needles, melts at 180°, and dissolves in potassium hydroxide solution. The second, $\begin{matrix}C(NHPh)\cdot CO \\ CBr—C(NPh)\end{matrix}\!\!>\!O$, crystallises from water in slender, brown needles melting at 188°; it dissolves in potassium hydroxide, and on the addition of hydrochloric acid to the solution copious evolution of carbon dioxide ensues. A third *isomeride*, $\begin{matrix}NHPh\cdot C—CO \\ CBr\cdot CO\end{matrix}\!\!>\!NPh$, is obtained by the action of aniline on dibromomaleic anhydride; it forms orange-yellow plates, melts at 192°, is readily soluble in hot alcohol or ether, and may be sublimed.

Anilinobromomaleic anhydride, $\begin{matrix}NHPh\cdot C—CO \\ CBr\cdot CO\end{matrix}\!\!>\!O$, crystallises from alcohol in golden-yellow needles. The three *chloro*-derivatives corresponding with the isomeric anilinobromo-anils have been prepared. The first turns brown at 175°, and melts at 188°, the second crystallises in golden plates and melts at 187°, and the third in prismatic, orange-red needles melting at 190°. *Anilinochloromaleic anhydride* is readily soluble in most organic solvents and begins to melt at 165°.

Anilinobromomaleic anhydride dianil,

$$C_{22}H_{16}ON_3Br,\ \begin{matrix}C(NHPh)\cdot C(NPh) \\ CBr——C(NPh)\end{matrix}\!\!>\!O(?),$$

obtained as a by-product in the preparation of methyl dianilinomaleate, crystallises from alcohol in orange-red plates melting at 186°.

A *trianilinobromodimaleic anhydride dianil*, $C_{38}H_{28}O_4N_5Br$, is obtained as a by-product in the preparation of dianilinomaleic anhydride. It has a brownish-red colour, dissolves readily in alcohol, melts at 160°, and does not crystallise well. The corresponding *chloro*-derivative turns black at 120°.

It has not been found possible to replace both bromine atoms in dibromomaleic acid by anilino-groups, but the change may be effected, although not readily, in the case of the anhydride or methyl ester.

Dianilinomaleic anhydride, $\begin{matrix}NHPh\cdot C\cdot CO \\ NHPh\cdot C\cdot CO\end{matrix}\!\!>\!O$, formed by adding aniline at 100—120° to dibromomaleic anhydride and subsequently heating at 130—140°, crystallises from boiling alcohol and melts at 231°.

Methyl dianilinomaleate crystallises in yellow prisms and melts at 172°, the *acid* assumes an orange colour at 140°, melts, and again solidifies, and then melts and decomposes at 175°. The *sodium* and *silver* salts were prepared.

When the methyl ester is fused with caustic potash, or when the sodium salt is fused with pure sodamide and a little potassium hydroxide, small amounts of indigo are obtained. J. J. S.

Preparation of Carbon Compounds containing Two Consecutive Double Linkings. ARRIGO MAZZUCCHELLI (*Atti R. Accad. Lincei*, 1905, [v], 14, i, 568—576).—The author describes unsuccessful attempts to synthesise compounds of the allene type, which have been but little studied and should prove of stereochemical interest.

Starting from ethyl diethylacetonedicarboxylate, he converted this, by the action of phosphorus pentachloride, into ethyl chlorodiethylglutaconate, $CO_2Et \cdot CHEt \cdot CCl:CEt \cdot CO_2Et$. All the means adopted for the removal of hydrogen chloride from the last compound led also to simultaneous substitution by hydroxyl. The action of alcoholic potassium hydroxide yielded ethylmalonic acid, butyric acid, and dipropyl ketone, whilst hydrochloric acid, acetates, and solutions of potassium hydroxide in water or methyl alcohol gave mixtures of the ethyl esters of chlorodiethylglutaconic and diethylacetonedicarboxylic acids and a certain amount of resin. Similar results were obtained with ethyl iododiethylglutaconate. T. H. P.

Solubility of Certain Metallic Tartrates in Water. H. CANTONI and Mlle. F. ZACHODER (*Bull. Soc. chim.*, 1905, [iii], 33, 747—754. Compare this vol., i, 14).—The solubilities of the tartrates of strontium, calcium, barium, copper, zinc, and lead have been determined at various temperatures between 0° and 85°, and the results are given in tables and curves in the original. J. J. S.

Formaldehyde and Formate Formation. HANS EULER and ASTRID EULER (*Ber.*, 1905, 38, 2551—2560).—The authors have studied the condition of formaldehyde in dilute alkaline solution. Formaldehyde behaves as a weak acid since, by the action of formaldehyde on alkali, the alkali salt of the aldehyde is formed, and this is partially hydrolysed in aqueous solution. A $N/1$ solution of the monosodium salt of formaldehyde contains about one-half of the salt as such, whilst the other half is resolved into free base and free formaldehyde. In dilute solution, the salt is a binary electrolyte; the strength (dissociation constant) of formaldehyde as an acid amounts to $1 \cdot 10^{-14}$ at 0°.

The formation of sodium or barium formate from formaldehyde and sodium hydroxide is a reaction of the second order. With a large excess of aldehyde, the reaction is one of the first order. The value of the constant falls slightly with the time. The reaction constants for barium hydroxide or sodium hydroxide are about the same, and fall somewhat with increase of the initial concentration of the aldehyde on account of the formation of the formaldehyde salt. In the formate formation examined, no oxidation occurred, since the reaction took place as quickly in an atmosphere of hydrogen as in oxygen. The reaction constant is tripled with a rise of temperature of 10°. Formate formation takes place more quickly with calcium hydroxide than with sodium or barium hydroxide.

A. McK.

Crystals of *s*-Tetrachloro*iso*propyl Formal. Louis Henry (*Bull. Acad. roy. Belg.*, 1905, 211—213).—Polemical. A reply to Cesàro (this vol., i, 570). P. H.

Dichloroacetyldextrin. A. Kldiaschwili (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 421—423).—*Dichloroacetyldextrin*, $C_8H_{10}O_6Cl_2$, is obtained by mixing rice starch with twice its weight of dichloroacetic acid in the cold and heating the whole in a reflux apparatus until the product gives no starch reaction with iodine even after saponification. It is deposited from acetone in a powdery mass, and ebullioscopic measurements of its solution in this solvent indicate a molecular weight corresponding with $6C_8H_{10}O_6Cl_2$. T. H. P.

Action of Ethylamine and *iso*Butylamine on Cæsium. Etienne Rengade (*Compt. rend.*, 1905, **141**, 196—198. Compare this vol., i, 174).—Cæsium dissolves in ethylamine to form an unstable, blue *cæsium-ethylammonium*, which decomposes into hydrogen and *cæsium-ethylamide*, NHEtCs; this crystallises in long, white needles, becomes yellow on exposure to air, inflames explosively when rapidly heated or on contact with moist air, and dissolves easily in ethylamine. It reacts with aqueous vapour in a vacuum to form ethylamine and cæsium hydroxide, and when slowly heated to 105—110° decomposes with formation of hydrogen, methane, and ethylene.

Cæsium dissolves in *iso*butylamine to form a colourless solution which yields hydrogen and, on evaporation of the excess of the base, *cæsium* iso*butylamide*, C_4H_9NHCs, which crystallises in white needles, is more stable than the methyl- or ethyl-amine compounds, becomes brown and inflames, but without detonation on contact with moist air, reacts with water in absence of air to form *iso*butylamine and cæsium hydroxide, and when heated to 110° undergoes a complex decomposition, with evolution of hydrogen, and finally of propane and propylene.

Cæsium-ethylamide is formed when cæsium-amide is dissolved in ethylamine and the solution evaporated; similarly, cæsium-ethylamine is converted into the amide and the *iso*butylamide by treatment with excess of ammonia and *iso*butylamine respectively. If a limited quantity of the ammonia or amine is used as solvent, an equilibrium is set up between the two possible amides and the two amines or the amine and ammonia. G. Y.

New Method for the Conversion of Primary Diamines into Chlorinated Amines and into Dichlorides. Julius von Braun and Carl Müller (*Ber.*, 1905, **38**, 2340—2348).—A 60 per cent. yield of $\alpha\epsilon$-dichloropentane, together with benzonitrile, is obtained by heating dibenzoylpentamethylenediamine with phosphorus pentachloride and distilling under atmospheric pressure. The product is distilled in steam, the nitrile hydrolysed with concentrated hydrochloric acid and the mixture again distilled in steam, when the dichloropentane passes over.

If the product is distilled under reduced pressure, a certain amount of benzoyl ϵ-chloroamylamine is obtained, and this, on hydrolysis, yields ϵ-chloroamylamine.

Other dichlorides and chloroamines may be obtained in a similar manner. A 60 per cent. yield of $\alpha\zeta$-dichlorohexane has been obtained from hexamethylenediamine. *ζ-Chlorohexylamine*, $NH_2\cdot[CH_2]_6\cdot Cl$, is an oil, and the *hydrochloride* a syrup; the *platinichloride* melts at 213—214° and the *picrate* at 115°. An aqueous suspension of the base gradually loses its alkaline properties when heated, as intramolecular transformations occur, one of the products being hexamethyleneimine, $(CH_2)_6\colon NH$. The best yield of the chlorinated base is obtained by reducing ε-phenoxyhexonitrile (this vol., i, 342) and replacing the phenoxy-group by chlorine.

$\alpha\eta$-Dichloroheptane distils at 120° under 28 mm. pressure, and with sodium phenoxide yields $\alpha\eta$-diphenoxyheptane melting at 53° (Solonina, Abstr., 1899, i, 561). Benzoyl-η-chloroheptylamine forms a snow-white, crystalline powder melting at 63°, and when hydrolysed with concentrated hydrochloric acid at 150° yields *η-chloroheptylamine hydrochloride* as a syrup. The *platinichloride* melts at 203°. The base is an oil with alkaline properties, and when heated with water undergoes intramolecular rearrangement. J. J. S.

Reduction of Ketoximes. New Synthesis of Amines. Amable Mailhe (*Compt. rend.*, 1905, **141**, 113—115. Compare this vol., i, 571).—When heated with finely-divided nickel at 150—180°, acetoxime yields a liquid which consists to the extent of about 1/3 of *iso*propylamine and of 2/3 of di*iso*propylamine. There is obtained also a small quantity of a liquid boiling at about 105° which is probably a mixture of di- and tri-*iso*propylamine.

Methyl ethyl ketoxime is reduced by finely-divided nickel at 150—200°, about 1/3 of the product being *sec*-butylamine, and about 2/3 di-*sec*-butylamine, with a small quantity of a liquid boiling below 160° and containing probably tri-*sec*-butylamine. Methyl ethyl ketoxime is reduced by nickel at 250° to ammonia, butane, and water, whilst with finely divided copper at 300° it forms the primary and secondary amines.

Di-sec-*butylamine* is a colourless liquid of characteristic odour, which boils at 132° under 758 mm. pressure, has a sp. gr. 0·7833 at 0°, and is extremely soluble in water. The *hydrochloride* is deliquescent; the *oxalate* melts at 104°.

The *hydrochloride* and *carbonate* of *sec*-butylamine crystallise in slender needles and are deliquescent.

Methyl *n*-propyl ketoxime is reduced by finely-divided nickel at 180—200°, 2/5 of the product being *sec*-amylamine and 3/5 di-*sec*-amylamine; at 250°, the reduction leads to the formation of ammonia, water, and the hydrocarbon. The primary and secondary amines are also formed by reduction by means of finely-divided copper. *sec*-Amylamine reacts with phenylcarbimide to form s-*phenyl*-sec-*amylcarbamide*, $NHPh\cdot CO\cdot NH\cdot CHMePr^{\alpha}$, which crystallises in prisms and melts at 120°.

Di-sec-*amylamine*, $NH(CHMePr^{\alpha})_2$, boils at 177° under 750 mm. pressure, has a sp. gr. 0·7916 at 0°, forms a deliquescent *hydrochloride*, and reacts with phenylcarbimide to form a-*phenyl*-bb-*di*-sec-*amylcarb*-

amide, $NHPh \cdot CO \cdot N(CHMePr^a)_2$, which crystallises in needles and melts at 134°. G. Y.

Synthesis of Hexamethylenediamine and Heptamethylenediamine from Piperidine. JULIUS VON BRAUN and CARL MÜLLER (*Ber.*, 1905, **38**, 2203—2210).—Benzoyl-ε-leucinonitrile,

$$NHBz \cdot [CH_2]_5 \cdot CN,$$

prepared from benzoyl-ε-chloroamylamine, $NHBz \cdot [CH_2]_4 \cdot CH_2Cl$ (Abstr., 1904, i, 918), gives on reduction with sodium and absolute alcohol an oil consisting of a mixture of the monobenzoyl derivative, $NHBz \cdot [CH_2]_6 \cdot NH_2$, of hexamethylenediamine with some of the base produced by hydrolysis; the oil is converted by benzoylchloride into dibenzoylhexamethylenediamine (αζ-dibenzoyldiaminohexane, Curtius and Clemm, Abstr., 1901, i, 68), $NHBz \cdot [CH_2]_6 \cdot NHBz$, which crystallises from alcohol. On heating the dibenzoyl derivative with concentrated hydrochloric acid, αζ-diaminohexane hydrochloride, identical with Curtius and Clemm's product, is obtained. The *benzenesulphonic* derivative, $SO_2Ph \cdot NH \cdot [CH_2]_6 \cdot NH \cdot SO_2Ph$, crystallises from alcohol and melts at 154°.

Pimelonitrile (Abstr., 1904, i, 970) is easily reduced by sodium and absolute alcohol, giving heptamethylenediamine, $NH_2 \cdot [CH_2]_7 \cdot NH_2$, identical with Solonina's product (*J. Russ. Phys. Chem. Soc.*, 1896, **28**, 558), prepared from suberic acid. The *benzenesulphonic* derivative, $NHBz \cdot [CH_2]_7 \cdot NHBz$, crystallises from methyl alcohol on adding ether and melts at 104°. In the formation of heptamethylenediamine from pimelonitrile, an imino-base, $[CH_2]_7 > NH$, is not formed, although the reduction of dicyanoethane or αγ-dicyanopropane gives rise to a cyclic imine as well as the aliphatic base. The tendency to form the imino-compound seems to cease when the carbon chain becomes 5-membered.

W. A. D.

Synthesis of a New Leucine. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Compt. rend.*, 1905, **141**, 115—117. Compare this vol., i, 32, 33; Ehrlich, Abstr., 1904, i, 560).—Two alcohols are formed by the fermentation of beet-root juice: *iso*butylcarbinol, related to leucine, and *sec*-butylcarbinol, related presumably in a similar manner to Ehrlich's *d-iso*leucine, which must therefore have the constitution $CHMeEt \cdot CH(NH_2) \cdot CO_2H$. An inactive leucine of this constitution has been prepared in the following manner.

Ethyl sec-*butylacetoacetate*, $CHMeEt \cdot CHAc \cdot CO_2Et$, formed by the action of *sec*-butyl iodide on ethyl sodioacetoacetate, is a colourless liquid which boils at 111—112° under 19 mm. pressure, has a sp. gr. 0·976 at 4°/0°, and with hydrazine forms a *pyrazolone* melting at 162° (corr.). When treated with nitrosyl sulphate in sulphuric acid solution, ethyl *sec*-butylacetoacetate yields *ethyl α-oximino-*sec-*butylacetate* [*α-oximino-β-methylvalerate*], $CHMeEt \cdot C(NOH) \cdot CO_2Et$, which is a viscid liquid boiling at 133—134° under 10 mm. pressure, and is easily hydrolysed by aqueous potassium hydroxide; the *acid* melts, decomposes, and sublimes at 164° (corr.). Along with the oximino-ester, there is formed a small quantity of *ethyl methylethylpyruvate*, which

yields a *semicarbazone* melting at 80—82°; the *acid* melts at 212° (corr.).

α-Amino-sec-*butylacetic* [*α-amino-β-methylvaleric*] *acid* is formed in a poor yield by reduction of ethyl α-oximino-*sec*-butylacetate with sodium amalgam. It is characterised by conversion into the p-*toluenesulphonate*, which melts at 141° (corr.). A 60 per cent. yield of the *ester*, $CHMeEt{\cdot}CH(NH_2){\cdot}CO_2Et$, is obtained by reduction of the oximino-ester with sodium amalgam in cooled alcoholic solution, neutralised from time to time by addition of alcoholic hydrochloric acid. It is a colourless liquid with a disagreeable odour, which boils at 90—92° under 15 mm. pressure and has a sp. gr. 0·957 at 4°/0°. With potassium cyanate in hydrochloric acid solution, it yields the crystalline *carbamido*-derivative, $CHMeEt{\cdot}CH(NH{\cdot}CO{\cdot}NH_2){\cdot}CO_2Et$, which melts at 81°. With benzoyl chloride in cooled pyridine solution, the amino-ester forms an oily *benzoyl* derivative, which boils at 213—214° under 19 mm. pressure, and is hydrolysed by alcoholic potassium hydroxide with formation of *α-benzoylamino-β-methylvaleric acid*, $CHMeEt{\cdot}CH(NHBz){\cdot}CO_2H$, which sinters at 115° and melts at 118°. The corresponding benzoyl derivative of Ehrlich's *d-iso*leucine sinters at 114° and melts at 116—117° (Abstr., 1903, i, 796).

G. Y.

Synthesis of Polypeptides. XII. Alanylalanine and its Derivatives. EMIL FISCHER and KARL KAUTZSCH (*Ber.*, 1905, **38**, 2375—2385. Compare Abstr., 1903, i, 465, 607, 799, 800; 1904, i, 652, 771, 867, 890, 917; this vol., i, 30, 31, 263).—*Alanylalanine*, $NH_2{\cdot}CHMe{\cdot}CO{\cdot}NH{\cdot}CHMe{\cdot}CO_2H$, is obtained by shaking alanine anhydride for some time with sodium hydroxide until the crystals which are first formed redissolve. The alkaline solution is neutralised with hydriodic acid, as the sodium iodide thus formed is readily soluble and the dipeptide practically insoluble in absolute alcohol. It crystallises from dilute alcohol in small needles, and melts and decomposes at 276° (corr.), its aqueous solution reacts feebly acid and dissolves cupric oxide, yielding a deep blue solution of the *cupric* salt, which is readily soluble in water and also moderately in alcohol.

Benzoylalanylalanine, $COPh{\cdot}NH{\cdot}CHMe{\cdot}CO{\cdot}NH{\cdot}CHMe{\cdot}CO_2H$, crystallises from water in colourless needles and melts at 203—204° (corr.). The *copper* salt, $(C_{13}H_{15}O_4N_2)_2Cu$, crystallises in microscopic, green needles, which seem to contain water of crystallisation. The *ethyl ester* melts at 114—116° (corr.). These products are probably stereoisomeric with those described by Curtius and van der Linden (Abstr., 1904, i, 883).

*α-Bromo*iso*hexoylalanylalanine*,

$$C_4H_9{\cdot}CHBr{\cdot}CO{\cdot}NH{\cdot}CHMe{\cdot}CO{\cdot}NH{\cdot}CHMe{\cdot}CO_2H,$$

is obtained by the action of α-bromo*iso*hexoyl chloride on an alkaline solution of alanine anhydride in two stereoisomeric modifications, which may be separated by repeated fractional crystallisation from ethyl acetate. The A compound, which is less readily soluble, crystallises in slender needles, softens at 180°, melts and decomposes at 191—193° (corr.), and dissolves readily in hot alcohol or acetic acid. One gram dissolves in about 80 c.c. of hot water or 35 c.c. of hot

ethyl acetate. The B compound melts at 160—163° and decomposes at a slightly higher temperature. One gram dissolves in 25 c.c. of boiling water or in 6 c.c. of boiling ethyl acetate.

Two stereoisomeric *leucylalanylalanines*,

$C_4H_9\cdot CH(NH_2)\cdot CO\cdot NH\cdot CHMe\cdot CO\cdot NH\cdot CHMe\cdot CO_2H$,

are obtained by the action of ammonia on the bromo-derivatives at 100°. The A compound sinters at 240° and melts and decomposes at 266° (corr.). It dissolves in hot water, dilute acids, or acetic acid, but is practically insoluble in the usual organic solvents. It gives a violet coloration with sodium hydroxide and cupric sulphate solutions. The *copper* salt has been obtained in the amorphous condition only. The B compound is amorphous, dissolves readily in water, and is not precipitated by alcohol. The *methyl ester* and *copper* salt are also amorphous.

a-Bromopropionylalanylalanine also exists in two modifications; the A compound, obtained by repeated crystallisation from water, melts and decomposes at 198—200° (corr.), dissolves sparingly in cold water, and moderately in hot ethyl acetate, acetone, or acetic acid. The B compound has not been obtained pure.

Dialanylalanine, $NH_2\cdot[CHMe\cdot CO\cdot NH]_2\cdot CHMe\cdot CO_2H$, crystallises in needles, melts and decomposes at 219° (corr.) when quickly heated, then solidifies, and melts and decomposes again at 256—261° (corr.). It dissolves readily in cold water, sparingly in alcohol, contains $\frac{1}{2}H_2O$, which it loses at 100°, and then forms a hygroscopic powder. It is tasteless and yields an amorphous *cupric* salt. J. J. S.

Chromous Sodium Thiocyanate. IWAN KOPPEL (*Zeit. anorg. Chem.*, 1905, **45**, 359—361).—When moist chromium acetate is gradually added, in absence of air, to a concentrated solution of sodium thiocyanate, it dissolves at first with production of a deep blue colour, and later a large yield of dark blue crystals having the composition $3NaCNS,Cr(CNS)_2,11H_2O$ separates. The crystals are easily decomposed by the action of oxygen or moisture.

The preparation of chromous chloride by the action of hydrochloric acid on small lumps of metallic chromium is recommended; the chromium is best prepared by the Goldschmidt aluminium process. Chromous chloride is thus obtained as a white, anhydrous product.

D. H. J.

Bromodialkylacetamides. KALLE & Co. (D.R.-P. 158220).—Bromodialkylacetamides of the formula $CBrRR'\cdot CO\cdot NH_2$ or $CBrRR'\cdot C(OH)\colon NH$ have a hypnotic action when R and R' = Et or Pr. Bromodimethylacetamide (α-bromo*iso*butyramide, Abstr., 1898, i, 10) has no such action.

To prepare these derivatives, the corresponding dialkylacetic acids are converted into the chlorides or bromides by phosphorus chloride or phosphorus and bromine respectively, and the amides prepared by passing ammonia into the ethereal solution or by adding to an excess of ammonia solution.

a-Bromo-a-ethylbutyryl chloride, $CBrEt_2\cdot COCl$, boils at 90—100° under 20 mm. pressure; *a-bromo-a-ethylbutyramide* melts at 64—65°

and dissolves in 115 parts of cold water, readily in alcohol, ether, benzene, or chloroform. *a-Bromo-a-propylvaleryl chloride*, $CBrPr_2\cdot COCl$, boils at 110—130° under 20 mm. pressure; the *amide* melts at 59—60° and is less soluble in water than the diethyl derivative. *a-Bromo-a-ethylvaleramide* is a pleasant-smelling oil. C. H. D.

isoCarbamides. JULIUS STIEGLITZ and R. W. NOBLE (*Ber.*, 1905, **38**, 2243—2244. Compare Stieglitz and McKee, Abstr., 1899, i, 594; 1900, i, 340, 431).—*O*-Alkyl esters of *iso*carbamide are readily prepared by warming cyanamide monohydrochloride (a mixture of cyanamide and cyanamide dihydrochloride) with a slight excess of the appropriate alcohol at about 60—70°.

O-*Ethyl*iso*carbamide hydrochloride* (*ethyl iminocarbamate hydrochloride*), $NH_2\cdot C(OEt)\colon NH,HCl$, forms well-defined crystals and gives a *platinichloride*, $C_6H_{18}O_2N_4PtCl_6$.

O-*Propyl*iso*carbamide hydrochloride* (*propyl iminocarbamate hydrochloride*) melts at 64° and decomposes at 121°. W. A. D.

Dimethylmethylenetrimethylene, $\genfrac{}{}{0pt}{}{CH_2}{CH_2}\!\!>C\colon CMe_2$. D. W. ALEXÉEFF (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 417—421).—*Dimethylmethylenetrimethylene* [β-propylene*cyclo*propane], $\genfrac{}{}{0pt}{}{CH_2}{CH_2}\!\!>C\colon CMe_2$, prepared by heating *cyclo*propyldimethylcarbinol in a sealed tube with acetic anhydride, has the odour of the naphthalene hydrocarbons, boils at 70·5—71° under 763 mm. pressure, has the sp. gr. 0·7532 at 20°/0°, and n_D 1·424. When the hydrocarbon is treated in the dark with a chloroform or carbon disulphide solution of bromine, two atoms of the latter are taken to satisfy the double linking and two more owing to the rupture of the carbon ring, while still more of the bromine brings about bromination accompanied by evolution of hydrogen bromide. T. H. P.

Purification of *o*-Nitrotoluene. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 158219. Compare Streng, Abstr., 1891, 1197; Schneider, Abstr., 1896, ii, 290).—*o*-Nitrotoluene freezes at −10·5°, but if cooled to −4°, crystals are obtained differing in form from those separating at −10·5°. It is thus possible to purify *o*-nitrotoluene by cooling the crude product to temperatures between −4° and −10° and removing the liquid portion by centrifugalisation when about one-half has crystallised. A mixture of *o*-nitrotoluene with 6 per cent. of *p*-nitrotoluene and 12 per cent. of *m*-nitrotoluene begins to crystallise at −9°. C. H. D.

Nitration of Aromatic Arylsulphonamides. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 157859).—It is not practicable to nitrate arylsulphonamides in sulphuric acid solution, but the reaction takes place smoothly when the amides are suspended in water and gently warmed with dilute nitric acid. The nitro-group always enters the para-position to the sulphonamide group, and secondary reactions do not occur.

The arylsulphonamides of benzene and toluene, derived from primary and secondary aromatic bases, are almost insoluble in water, but dissolve readily in alcohol, ether, or benzene. Those derived from primary bases form crystalline sodium salts. The *p*-nitro-derivatives are similar, those derived from primary bases form yellow sodium salts. The following new compounds are described:

Product from toluene-*p*-sulphonic chloride and	m. p.	*p*-Nitro-compound. m.p.
Aniline	103°	191°
o-Toluidine	108	172
o-Anisidine	127	175
o-Chloroaniline	105	164
p-Xylidine	119	185
o-Amino-*p*-cresol ethyl ether	112	150
Ethylaniline	87	107
α-Naphthylamine	156	185
Product from benzenesulphonic chloride and		
o-Anisidine	89	181
o-Chloroaniline	127	161

C. H. D.

Behaviour of Aromatic Sulphinic Acids towards Mercuric Salts. Walter Peters (*Ber.*, 1905, **38**, 2567—2570).—Attempts have been made to prepare isomeric metallic salts of aromatic sulphinic acids; for example, R·SO·OM and $R·SO_2·M$ (M = metal), corresponding with Otto's isomeric esters (Abstr., 1880, 810; 1885, 1232), but without success.

Mercuric p-*toluenesulphinate*, $(C_6H_4Me·SO·O)_2Hg$, is obtained when an aqueous solution of mercuric acetate is added to a dilute alcoholic solution of the sulphinic acid at 0°. Although soluble in pyridine and in hot nitric or acetic acid, it has not been obtained in a crystalline form.

When an aqueous alcoholic solution of the sulphinic acid and mercuric chloride in molecular proportions is heated just to boiling, mercury *p*-tolyl chloride (Abstr., 1882, 732) is formed.

Mercury phenyl chloride has been prepared in a similar manner.

J. J. S.

Action of Acetylene Tetrabromide and Aluminium Chloride on Toluene. James Lavaux (*Compt. rend.*, 1905, **141**, 204—206. Compare this vol., i, 43, 125; Anschütz and Romig, Abstr., 1885, 768).—The solid product formed by the interaction of acetylene tetrabromide, aluminium chloride, and toluene, consists of a mixture of *A*- and *B*-dimethylanthracenes, melting at 240° and 244·5° respectively, with traces of β-methylanthracene. The melting point 225°, observed by Anschütz and Romig, is that of a mixture of about equal parts of *A*- and *B*-dimethylanthracenes. The yield of dimethylanthracenes is more constant, and is increased from 10—20 to 42 per

cent. of the theoretical, and at the same time the formation of resinous products is diminished if the reacting mixture is shaken during the whole course of the reaction. The liquid product contains, in addition to unchanged toluene, benzene, xylene, trimethylbenzene, and other benzene homologues. G. Y.

Triphenylmethyl. XII. Moses Gomberg and Lee H. Cone (*Ber.*, 1905, **38**, 2447—2458. Compare Abstr., 1901, i, 77, 319, 638, 690; 1902, i, 534, 600, 754; 1903, i, 81, 244; 1904, i, 658, 988; this vol., i, 426).—Triphenylmethyl forms additive compounds of the type $CRR'{:}O(CPh_3)_2$, with the following ketones and ethers: methyl ethyl, diethyl, methyl propyl, methyl butyl, and dipropyl ketones; acetylacetone; methyl hexyl ketone; acetophenone; diethyl, methyl propyl, and ethyl propyl ethers; methylal; phenetole; anisole; benzyl ethyl ether; *o*-tolyl methyl ether. The composition of the additive compounds is determined usually by decomposition at 110—130°, of the additive compounds with phenetole and anisole at 110—130° in a vacuum; the additive compounds with the less volatile ketones and ethers are oxidised to triphenylmethyl peroxide. The low percentages of ketones and ethers found for the additive compounds with the ketones and ethers of high boiling point are due probably to superficial decomposition during the necessary washing with light petroleum. The hydrocarbon does not form an additive compound with acetone or *iso*butaldehyde.

No additive compound of triphenylmethyl and acetonitrile could be obtained. With propionitrile, the *compound* $CEt{:}N(CPh_3)_2$ is formed in transparent, colourless crystals. With benzonitrile, the hydrocarbon forms an *additive compound*, which crystallises in thin, white needles, is stable in an indifferent atmosphere, and has probably the constitution $(CPh_3)_2C_6H_5{\cdot}C{:}N(CPh_3)_2$.

On adding warm alcohol to a solution of triphenylmethyl in chloroform and cooling the mixture, a crystalline product is obtained, which, after repeated washing with absolute alcohol and light petroleum and drying in a vacuum, loses 6·7 per cent. at 110°, 72 per cent. of the volatile part consisting of chloroform. On adding ethyl or *iso*propyl alcohol to the solution of triphenylmethyl in carbon disulphide, crystals are obtained containing 7·8—10·35 per cent. of carbon disulphide and only traces of alcohol. Crystals obtained by the precipitation of triphenylmethyl from its solution in carbon disulphide by adding light petroleum lose 0·14—0·5 per cent. at 110°, the volatile part consisting chiefly of carbon disulphide. The formation of additive compounds by addition of two triphenylmethyl groups to an unsaturated linking or to an atom which can act with a higher valency agrees with the peroxide and iodide formation in pointing to the constitution CPh_3. If Ullmann and Borsum's compound is benzhydryltetraphenylmethane (Tschitschibabin, this vol., i, 125), its formation from Gomberg's triphenylmethyl is not explained by supposing the latter to be hexaphenylethane. Moreover, triphenylmethyl is colourless in the solid state, but forms intensely yellow solutions, a behaviour not in agreement with the properties of saturated hydrocarbons.

The chemical behaviour of triphenylmethane cannot be explained by

Jacobson's formula (this vol., i, 186), which, however, takes into account the dimolecular state of triphenylmethyl. G. Y.

Phenylchrysofluorene. Fritz Ullmann and Anna Mourawiew-Winigradoff (*Ber.*, 1905, 38, 2213—2219).—Diphenyl-α-naphthylcarbinol, $C_{10}H_7 \cdot CPh_2 \cdot OH$ (Acree, Abstr., 1904, i, 360), is easily prepared from phenyl α-naphthyl ketone and magnesium phenyl bromide, and on reduction gives diphenyl-α-naphthylmethane. On heating the carbinol with aniline hydrochloride and glacial acetic acid, with acetic acid containing sulphuric acid or zinc chloride, or with alcoholic zinc chloride, *phenyl chrysofluorene*, $\begin{matrix} C_{10}H_6 \\ | \\ C_6H_4 \end{matrix}\!\!>\!CHPh$, is obtained; it crystallises from glacial acetic acid in long, lustrous needles, melts at 195·5°, and, on oxidation with sodium dichromate in acetic acid solution, gives *o*-benzoylbenzoic acid. *Phenyl chrysofluorenol*, $\begin{matrix} C_{10}H_6 \\ | \\ C_6H_4 \end{matrix}\!\!>\!CPh \cdot OH$, obtained by the action of magnesium phenyl bromide on chrysofluorenone (Graebe, this vol., i, 82), crystallises from benzene or carbon tetrachloride on adding light petroleum in large, lustrous, slightly yellow prisms and melts at 149·5°. On reduction with zinc dust in glacial acetic acid, phenylchrysofluorene is obtained, identical with the substance already described.

Aminodiphenylchrysofluorene, $\begin{matrix} C_{10}H_6 \\ | \\ C_6H_4 \end{matrix}\!\!>\!CPh \cdot C_6H_4 \cdot NH_2$, obtained by heating chrysofluorenol with aniline hydrochloride and glacial acetic acid, separates in small, colourless crystals and melts at 215°.

Diphenyl-β-naphthylcarbinol, $C_{10}H_7 \cdot CPh_2 \cdot OH$, cannot be prepared from methyl β-naphthoate and magnesium phenyl bromide, but is easily obtained by the action of the latter on phenyl β-naphthyl ketone; it crystallises from a mixture of ether and light petroleum in large prisms, melts at 115·5°, and, when heated with glacial acetic acid and concentrated hydrochloric acid, gives *phenyl-phenylene β-naphthylenemethane*, $\begin{matrix} C_{10}H_6{}^{\beta} \\ | \\ C_6H_4 \end{matrix}\!\!>\!CHPh$, crystallising from benzene and melting at 137°. W. A. D.

Acetylation in Aqueous Solutions. Auguste Lumière, Louis Lumière, and Henri Barbier (*Bull. Soc. chim.*, 1905, [iii], 33, 783—787).—12·3 grams of acetic anhydride dissolve in 120 c.c. of cold water, yielding a solution which readily acetylates amino- and imino-compounds. Thus, aniline or a solution of aniline in dilute acetic acid, when shaken with the anhydride solution, gives an almost theoretical yield of acetanilide. A solution of aniline hydrochloride gives no precipitate when shaken with the anhydride solution, unless sodium acetate is added.

The following acetyl derivatives have been prepared by this method: acetanilide, *o*-acetotoluidide, acetoxylidide, acetomethylanilide, aceto-*p*-phenetidide, acetylphenylhydrazine, diacetyl-*p*-phenylenediamine, *o*-acetylaminophenol, *p*-acetylaminophenol, 2 : 4-diacetyldiaminophenol, acetylanthranilic acid, acetylphenylglycine. Acetyl-*p*-hydroxyphenyl-

glycine, $OH\cdot C_6H_4\cdot NAc\cdot CH_2\cdot CO_2H$, which cannot be obtained by boiling hydroxyphenylglycine with acetic anhydride, is readily prepared by dissolving hydroxyphenylglycine in sodium carbonate solution and shaking with the aqueous solution of acetic anhydride. It crystallises from water in colourless prisms melting at 203° and dissolves readily in alcohol or hot water, but only sparingly in ether, chloroform, or benzene. J. J. S.

Crystalline and Liquid Modifications of Formanilide and *p*- and *o*-Formotoluidides. E. I. Orloff (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 439—442).—The interaction of formylglycerol and aniline yields two modifications of formanilide: (1) a crystalline form, melting at 245°, to which the author gives the constitution $\begin{matrix} C_6H_5\cdot NH \\ | \\ H\cdot C{:}O \end{matrix}$; (2) a liquid form, $\begin{matrix} C_6H_5\cdot N \\ \| \\ H\cdot C\cdot OH \end{matrix}$. The ordinary form melting at 46° has the structure $\begin{matrix} C_6H_5\cdot N \\ \| \\ OH\cdot C\cdot H \end{matrix}$. The second and third modifications give the compound $NPhNa\cdot CHO$ when treated with sodium hydroxide, but the tautomeric form resembles acetanilide in yielding no sodium derivative.

Similar modifications of *p*- and *o*-formotoluidides were obtained. T. H. P.

Action of Ethyl Chloroacetate on the Magnesium Halogen Compound of *o*-Toluidine. F. Bodroux (*Compt. rend.*, 1905, **141**, 195—196. Compare this vol., i, 427).—Ethyl chloroacetate reacts with the magnesium iodide derivative of *o*-toluidine in ethereal solution to form iodoaceto-*o*-toluidide. If, as sometimes happens, the magnesium halogen compound undergoes spontaneous coagulation, the yield of iodoaceto-*o*-toluidide is very small, the chief product being ethyl iodoacetate.

Iodoaceto-o-toluidide crystallises in long, white needles and melts and decomposes at 142°.

The action of ethyl chloroacetate on the magnesium bromide derivative of *o*-toluidine leads to the formation of chloroaceto-*o*-toluidide in a 50 per cent. yield, along with a compound which melts below 95° and has not been obtained in a state of purity.

Dichloroaceto-o-toluidide, formed by the action of ethyl dichloroacetate on the magnesium bromide or, along with a small quantity of an iodine compound, on the magnesium iodide derivative of *o*-toluidine, crystallises in long, white needles and melts at 134°. *Trichloroaceto-o-toluidide*, formed in the same manner from ethyl trichloroacetate, crystallises in long, white needles and melts at 95°. G. Y.

Condensation Products of Primary Aromatic Amines with Formaldehyde. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 158543).—It was shown by Pulvermacher (Abstr., 1892, 1450) that the nitroanilines react with formaldehyde in alcoholic solution to form methylene derivatives. It is found that formaldehyde also reacts with salts of the aromatic nitro-amines in aqueous solution. Thus, 4-nitro-2-aminotoluene hydrochloride and formaldehyde yield

the *compound* $CH_2(NH\cdot C_6H_3Me\cdot NO_2)_2$, which crystallises from alcohol and acetic acid in glistening, yellow needles and melts at 230°; it is insoluble in cold dilute acids. The corresponding *compound* from *o*-nitro-*p*-toluidine forms orange needles and melts at 254°.

C. H. D.

1 : 1′-Dichloro-2 : 2′-dinaphthylamine. WLADIMIR G. SCHAPOSCHNIKOFF and F. GOLEFF (*Zeit. Farb. Text. Ind.*, 1905, 4, 281—283).—On adding $\beta\beta$-dinaphthylamine dissolved in glacial acetic acid to quinonedichlorodi-imine dissolved in the same solvent, keeping the temperature below 45°, 1 : 1′-*dichloro*-2 : 2′-*dinaphthylamine*, $NH(C_{10}H_6Cl)_2$, is obtained; it crystallises from glacial acetic acid or benzene in needles, melts at 145°, and on heating with lime gives rise to naphthacarbazole. A small quantity of a *dye*, probably

$$NH_2\cdot C_6H_3 \lessdot \begin{matrix} N\text{———————} \\ NCl(C_{10}H_7) \end{matrix} > C_{10}H_6,$$

is also formed; it gives a red *hydrochloride* crystallising in needles, is easily acetylated and diazotised.

From the foregoing experiments, dichloroquinonedi-imine appears capable of acting as a chlorinating agent.

W. A. D.

Action of Sulphur on the Organo-magnesium Derivatives of *p*-Bromo-anisole and -phenetole. F. TABOURY (*Bull. Soc. chim.*, 1905, [iii], 33, 836—839. Compare Abstr., 1903, i, 748; 1904, i, 493).—*p*-Methoxy- and *p*-ethoxy-thiophenols (Abstr., 1892, 1089) are formed by the action of sulphur, followed by acidified water, on the magnesium derivatives of *p*-bromo-anisole and -phenetole. The corresponding disulphides are not formed as by-products, but may be obtained by the action of hydrogen peroxide on the thiophenols.

Acyl chlorides react with these magnesium compounds yielding aryl thiocarboxylates. p-*Methoxyphenyl thioacetate*, $OMe\cdot C_6H_4S\cdot COMe$, is an oil distilling at 163—166° under 12 mm. pressure. The corresponding *thiobenzoate* crystallises from alcohol in slender needles melting at 99—100°. p-*Ethoxyphenyl thioacetate* melts at 41—42° and the corresponding *thiobenzoate* at 106°.

Alkyl haloids react with the magnesium compounds yielding alkyl sulphides. *Benzyl* p-*methoxyphenyl sulphide*, $OMe\cdot C_6H_4\cdot S\cdot CH_2Ph$, melts at 45—46°, and *benzyl* p-*ethoxyphenyl sulphide* at 43—44°.

J. J. S.

Phenylation of Phenols. FRITZ ULLMANN, PAUL SPONAGEL [and, in part, STEIN] (*Ber.*, 1905, 38, 2211—2212).—When potassium phenoxide is heated with bromobenzene for twelve hours at 180—210°, the yield of diphenyl ether obtained is only 0·9 per cent. of the theoretical; on adding a small quantity of copper, however, and heating for two hours at 210—230°, 87 per cent. of the theoretical quantity of diphenyl ether is obtained. *o*-Methoxydiphenyl ether, $OPh\cdot C_6H_4\cdot OMe$, may be prepared similarly from guaiacol, and phenoxybenzoic acid from salicylic acid. Bromobenzene may also in this method of preparation be replaced by its homologues. m-*Nitrodiphenyl ether*, $OPh\cdot C_6H_4\cdot NO_2$, prepared from *m*-bromonitrobenzene, is

a yellow oil which boils at 198—200° under 14 mm. pressure. From phenol and *p*-dibromobenzene, *quinol diphenyl ether*, $C_{18}H_{14}O_2$, is obtained; it melts at 77° and boils at 371—372° under 720 mm. pressure. *Phloroglucinol triphenyl ether*, obtained from *s*-tribromobenzene, melts at 110°. W. A. D.

Condensation of Chloral with Aromatic Hydrocarbons under the Influence of Aluminium Chloride. ADOLPHE DINESMANN (*Compt. rend.*, 1905, **141**, 201—203. Compare Combes, Abstr., 1884, 837; Fritsch, Abstr., 1897, i, 568).—The action of chloral on benzene, toluene, *p*-xylene, and anisole in presence of aluminium chloride leads to the formation of the corresponding phenyltrichloromethylcarbinols.

Phenytrichloromethylcarbinol, formed by this reaction, melts at 37°, boils at 145° (corr.) under 15 mm. pressure, and is identical with Jocitsch's compound, prepared by the action of chloral on magnesium phenyl bromide (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 96). It reduces ammoniacal silver nitrate and Fehling's solution, yields with benzoyl chloride the *benzoyl* derivative, $OBz \cdot CHPh \cdot CCl_3$, which crystallises in needles and melts at 97—98°, and is reduced by zinc dust and acetic acid to dichlorostyrene (Jocitsch and Faworsky, Abstr., 1899, i, 786). With fuming nitric acid, dichlorostyrene yields a *nitro*-derivative which melts at 93° and is reduced by zinc and acetic acid to an *amine* melting at 99—100° and an *azo*-compound crystallising in red lamellæ and melting at 146—147°.

p-Tolyltrichloromethylcarbinol, prepared by condensation of chloral with toluene, melts at 63—64°, boils at 154—156° under 13·5 mm. pressure, and is identical with Jocitsch's compound formed from chloral and magnesium *p*-tolyl bromide (*loc. cit.*). The *acetate* melts at 107—108°; the *benzoate* melts at 100—101°. On oxidation with chromic acid, the carbinol yields a mixture of the corresponding ketone with unchanged carbinol, which, when treated with alkali hydroxides, is decomposed with formation of chloroform and *p*-toluic acid.

p-*Xylyltrichloromethylcarbinol*, $C_8H_9 \cdot CH(OH) \cdot CCl_3$, melts at 61—61·5°. The *acetate* melts at 85—87°; the *benzoate* melts at 112·5—113·5°.

p-*Methoxyphenyltrichloromethylcarbinol*, $OMe \cdot C_6H_4 \cdot CH(OH) \cdot CCl_3$, melts at 55—56°, boils at 184—186° under 16 mm. pressure, and forms an *acetate* melting at 79—81°. When oxidised with chromic acid and treated with potassium hydroxide, the carbinol yields chloroform and anisic acid. G. Y.

[*p*-Methoxyphenylethylcarbinol.] AUGUST KLAGES (*Ber.*, 1905, **38**, 2219—2222).—Polemical (compare Abstr., 1904, i, 487, and this vol., i, 344; Hell, this vol., 436). W. A. D.

Preparation of ω-Cyanomethylanthranilic Acid. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 158346).—Formaldehyde combines with anthranilic acid in aqueous suspension or ethereal solution to form a *compound*, separating in yellowish-white crystals, melting and decomposing at about 145—150°, insoluble in cold dilute alkalis or

acids, readily soluble in acetone. The product, which shows strong triboluminescence, is not a Schiff's base. Potassium cyanide or hydrocyanic acid reacts with it, yielding ω-cyanomethylanthranilic acid. C. H. D.

Hydroxymethyl Derivatives of Amides. Alfred Einhorn (D.R.-P. 158088).—The hydroxymethyl derivatives of amides, $RCO\cdot NH\cdot CH_2\cdot OH$ (this vol., i, 344), may be prepared by the action of formaldehyde on amides in the presence of acid condensing agents instead of alkalis, if precautions are taken to prevent the reaction from extending further to the formation of methylenediamine derivatives. Thus, when benzamide and formaldehyde are warmed with dilute sulphuric acid at 25° until completely dissolved, and immediately precipitated by sodium acetate, hydroxymethylbenzamide is obtained. The preparation of hydroxymethylsalicylamide is also described. C. H. D.

Claisen's Cinnamic Acid Synthesis. Arthur Michael (*Ber.*, 1905, 38, 2523—2524).—A reply to Stoermer and Kippe (this vol., i, 526). A. McK.

Formation of Liebermann's *iso*Cinnamic Acid by the Resolution of *allo*Cinnamic Acid with Brucine. Emil Erlenmeyer, jun. (*Ber.*, 1905, 38, 2562—2565. Compare this vol., i, 193). —A very small amount of *allo*cinnamic acid is formed when cinnamaldehyde is incompletely oxidised. When a mixture of brucine and *allo*cinnamic acid is crystallised from absolute alcohol, a crystalline *brucine* salt melting at 151° is obtained. The yield is about 50 per cent., and the salt, when decomposed with dilute sulphuric acid, yields Liebermann's *iso*cinnamic acid (Abstr., 1890, 494, 620), which crystallises from light petroleum in large, monoclinic crystals

$$[a : b : c = 0{\cdot}5555 : 1 : 0{\cdot}4053\ ;\ \beta = 70°8']$$

melting at 58—59°. Complete crystallographic data are given. The mother liquor from the crystalline salt melting at 151° yields a syrup which solidifies and then melts at 110—120°; this product is under investigation.

Liebermann's *iso*cinnamic acid appears to be a component of *allo*-cinnamic acid. Cinnamic acid itself yields but one brucine salt. Erlenmeyer's *iso*cinnamic acid may be obtained when an aqueous sulphuric acid solution of the allo-acid is kept for some time. J. J. S.

p-Chloroacetylphenoxyacetic Acid and Ethyl p-Chloroacetylphenylacetate. Franz Kunckell (*Ber.*, 1905, 38, 2609—2611).—Acyl groups, for example, chloroacetyl, can be readily introduced into phenylacetic and phenoxyacetic acids and their esters by means of the Friedel-Crafts synthesis, using carbon disulphide as diluent.

p-*Chloroacetylphenoxyacetic acid*, $CH_2Cl\cdot CO\cdot C_6H_4\cdot O\cdot CH_2\cdot CO_2H$, crystallises from hot water in glistening plates, melts at 146—147°, and is readily soluble in ether, alcohol, or chloroform. The *sodium*, *silver*, and *cupric* salts have been prepared.

Ethyl p-*chloroacetylphenylacetate*, $CH_2Cl \cdot CO \cdot C_6H_4 \cdot CH_2 \cdot CO_2Et$, crystallises from a mixture of ether and light petroleum in colourless needles, melts at 56—58°, and dissolves readily in alcohol or ether.

J. J. S.

Derivatives of Indoxylic Acid. CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 158089).—Phenylglycinecarboxylic esters are converted into indoxylic esters by heating with sodium ethoxide (Vorländer and Schilling, Abstr., 1898, i, 682). It is found that esters or amides of the general formula $R'CO \cdot C_6H_4 \cdot NR''' \cdot CH_2 \cdot COR''$ (where R′ and R″ are alkyloxy-, amino-, or alkylamino-groups, and R‴ is hydrogen or acyl) are readily converted into indoxylic esters when heated with sodamide or its substituted derivatives in presence of an indifferent liquid at temperatures below 130°. If fused, indoxyl is formed (Abstr., 1903, i, 632). Thus an almost theoretical yield of ethyl indoxylate is obtained on heating ethyl phenylglycine-*o*-carboxylate with sodioacetanilide and xylene at 125—130°.

Ethyl p-*bromophenylglycine*-o-*carboxylate* melts at 97° and when heated with sodioacetanilide and xylene yields *ethyl bromoindoxylate*, separating from dilute alcohol in green crystals and melting at 152—154°. Other preparations are described in detail. C. H. D.

Isolation of Amino-acids. CARL NEUBERG and ALBERT MANASSE (*Ber.*, 1905, **38**, 2359—2366. Compare E. Fischer and Bergell, Abstr., 1903, i, 24; Siegfried, this vol., i, 59; Hinsberg, Abstr., 1901, i, 128).—Amino-acids yield well-crystallised additive products with α-naphthylcarbimide, and the yield is quantitative when the carbimide is shaken for a few minutes with an alkaline solution of the amino-acid without artificial cooling, and then left for $\frac{1}{2}$—$\frac{3}{4}$ hour. The solution is filtered to remove dinaphthylcarbamide and the filtrate acidified, when the naphthylhydantoic acid is precipitated. Good results have been obtained with α- and β-amino-acids, amino-aldehydes, aminohydroxy-acids, diamino-acids, and peptides. Amino-acids may be estimated in urine in a similar manner after the removal of albumin. Hippuric acid does not react with the naphthylcarbimide.

α-*Naphthylcarbimideglycine* (α-*naphthylhydantoic acid*),

$$CO_2H \cdot CH_2 \cdot NH \cdot CO \cdot NH \cdot C_{10}H_7,$$

crystallises from alcohol in colourless needles and melts at 190·5—191·5°. It dissolves in alkalis and yields an insoluble *barium* salt.

α-*Naphthylcarbimide*-r-*alanine*, $CO_2H \cdot CHMe \cdot NH \cdot CO \cdot NH \cdot C_{10}H_7$, melts at 198°, and its *barium* salt is moderately soluble in water. The following have also been prepared:

Acid.	M. p. of α-naphthylcarbimide.
r-α-Amino-n-butyric acid	194—195°.
Leucine	163·5
l-Tyrosine	205—206
Glycylglycine	217
Glutamic acid	236—237
Cystine	Alkali salts sparingly soluble.

Diphenylcarbamide chloride reacts with amino-acids in the presence of alkali, yielding substituted carbamides. The reaction proceeds readily on warming. Diphenylhydantoic acid (*glycinediphenylcarbamide*), $CO_2H \cdot CH_2 \cdot NH \cdot CO \cdot NPh_2$, crystallises in glistening, hexagonal plates and melts at 144·5°. J. J. S.

Use of Phenyl Ether in the Friedel-Crafts Reaction. HERMANN KIPPER (*Ber.*, 1905, **38**, 2490—2493).—Phenyl ether reacts with acid chlorides or acid anhydrides in molecular proportions in the presence of aluminium chloride.

p-*Phenoxyacetophenone*, $OPh \cdot C_6H_4 \cdot COMe$, prepared from phenyl ether, acetyl chloride, and aluminium chloride, boils at 318—325° and melts at 45° (corr.). It forms an intensely yellow solution with sulphuric acid.

β-p-*Phenoxybenzoylpropionic acid*, $OPh \cdot C_6H_4 \cdot CO \cdot C_2H_4 \cdot CO_2H$, prepared from phenyl ether, succinic anhydride, and aluminium chloride, separates from aqueous alcohol in glistening leaflets and melts at 117° (corr.). Its solution in sulphuric acid is intensely yellow.

p-*Phenoxybenzophenone*, $OPh \cdot C_6H_4 \cdot COPh$, prepared from phenyl ether, benzoyl chloride, and aluminium chloride, separates from aqueous alcohol in glistening needles and melts at 71° (corr.). Its solution in sulphuric acid is yellow.

p-*Phenoxybenzoylbenzoic acid*, $OPh \cdot C_6H_4 \cdot CO \cdot C_6H_4 \cdot CO_2H$, prepared from phenyl ether, phthalic anhydride, and aluminium chloride, separates from aqueous alcohol in glistening needles and melts at 163·5° (corr.). Its solution in sulphuric acid is red. A. McK.

Hydroxyanthraquinoneglycollic [Anthraquinoneoxyacetic] Acids and their Esters. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 158277).—The metallic derivatives of hydroxyanthraquinones react with alkyl chloroacetates or bromoacetates to form anthraquinoneoxyacetic esters corresponding with phenoxyacetic esters. The crystalline esters are readily saponified by alkali hydroxides, and the acids may be precipitated from solutions of the salts thus obtained.

Ethyl anthraquinone-2-oxyacetate, $C_6H_4 <^{CO}_{CO}> C_6H_3 \cdot O \cdot CH_2 \cdot CO_2Et$, prepared by boiling sodium 2-hydroxyanthraquinone with ethyl chloroacetate in a reflux apparatus, forms yellowish-white needles, melts at 135°, and distils without decomposition; it dissolves readily in benzene or acetic acid, sparingly in alcohol or ether. Sulphuric acid dissolves it to an orange solution. *Sodium anthraquinone-2-oxyacetate* is crystalline and dissolves in water to a pale yellow solution. The *acid* separates from glacial acetic acid as a yellowish-white powder, melts at 234—235°, and dissolves less readily in organic solvents than the ethyl ester.

Ethyl anthraquinone-1-oxyacetate forms yellow needles and melts at 174—175°. The corresponding *ester* from alizarin crystallises from benzene in orange leaflets and melts at 165—166°. It yields a red, sparingly soluble *sodium* salt, which is hydrolysed on boiling to the

readily soluble *sodium* salt of the glycollic acid. The *acid* separates from acetic acid in orange crystals and melts at 267—268°.

The *diglycollic* ester from the tetrasodium derivative of anthrachrysone and ethyl bromoacetate forms yellow needles and melts at 227—229°, and on hydrolysis yields 4 : 8-*dihydroxyanthraquinone*-2 : 6-*dioxydiacetic acid*,

$$CO_2H\cdot CH_2\cdot C_6H_2(OH)<{}^{CO}_{CO}>C_6H_2(OH)\cdot CH_2\cdot CO_2H,$$

which melts above 290° and dissolves very sparingly in organic solvents. C. H. D.

Derivatives of β-Aminoethyl- and of α-Aminopropyl-alcohol. SIEGMUND GABRIEL (*Ber.*, 1905, 38, 2389—2404. Compare Abstr., 1890, 472).—The reaction between γ-bromopropylphthalimide and alkalis does not consist of the mere replacement of bromine by hydroxyl, but in the following series of transformations :

$$C_6H_4<{}^{CO}_{CO}>N\cdot C_3H_6Br \longrightarrow C_6H_4<{}^{CO_2K}_{CO\cdot NH\cdot C_3H_6Br} \longrightarrow$$

Potassium γ-bromopropylphthalamate.

$$C_6H_4<{}^{CO_2H}_{CO\cdot O\cdot C_3H_6\cdot NH_2} \longleftarrow C_6H_4<{}^{CO\cdot NH\cdot CH_2}_{CO-O-CH_2}>CH_2.$$

γ-Aminopropyl hydrogen phthalate. γ-Hydroxypropylphthalamic anhydride.

γ-*Aminopropyl hydrogen phthalate* is formed when the bromo-compound is heated with alcoholic potassium hydroxide for 15 minutes. It crystallises with $1H_2O$ in rhombic plates, and when quickly heated melts at 168—169°, but water is eliminated at the same time, and γ-hydroxypropylphthalimide, melting at 75°, is formed. It dissolves in both acids and alkalis ; the *hydrochloride*, $C_{11}H_{13}O_4N,HCl$, begins to sinter at 160° and melts to a clear liquid at 163·5°. The *platinichloride* crystallises in flat needles, and when slowly heated melts at 204—205°.

The *methyl* ester, $CO_2Me\cdot C_6H_4\cdot CO_2\cdot C_3H_6\cdot NH_2$, is an oil which yields a strongly alkaline aqueous solution and a *hydrochloride* melting at 124—125°.

When bromopropylphthalimide is shaken with cold 4*N* aqueous potassium hydroxide and then acidified, γ-*bromopropylphthalamic acid* is obtained. It crystallises from ethyl acetate in flat needles and melts at 107—108°. When warmed with hydrobromic acid of different concentrations, it is either transformed into bromopropylphthalamide or hydrolysed to bromopropylamine hydrobromide and phthalic acid. With alcoholic potash, it is ultimately converted into γ-aminopropyl hydrogen phthalate, but yields as an intermediate product *anhydro-γ-hydroxypropylphthalamic acid*, which is readily purified by conversion into the sparingly soluble nitrosoamine (see following abstract). The *hydrochloride*, $C_{11}H_{11}O_3N,HCl$, of the anhydro-base melts at 137°, dissolves extremely readily in water and moderately in alcohol. It is readily hydrolysed to the hydrochloride of γ-aminopropyl hydrogen phthalate when its aqueous solution is warmed, but in the presence of a relatively large amount of alkali the base is comparatively stable. The *aurichloride*, $C_{11}H_{11}O_3N,HAuCl_4$,

crystallises in golden-yellow, flat needles and melts at 198—199°, the *platinichloride* melts and decomposes at 193°, and the *picrate* melts at 182°. The *base* crystallises in glistening, felted needles, melts at 136°, and is readily soluble in water but insoluble in ether. It readily combines with water forming the *hydrate*, $C_{11}H_{11}O_3N,3H_2O$, which crystallises in glistening plates or prisms melting at 72—73°. When distilled, the hydrochloride is converted into *γ-chloropropylphthalimide*, $C_6H_4{<}{}^{CO}_{CO}{>}N{\cdot}C_3H_6Cl$, which crystallises from light petroleum in prisms melting at 67—68°.

The transformation of β-bromoethylphthalimide into the corresponding β-hydroxy-compound proceeds in a manner similar to that described for the γ-bromopropylphthalimide. *β-Bromoethylphthalamic acid*,

$$CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CH_2Br,$$

crystallises from ethyl acetate in compact needles melting at 125·5°.

The compound previously described as the hydrochloride of hydroxyethylphthalamic acid (Abstr., 1888, 440) is shown to be the *hydrated hydrochloride* of the *imino-base*, namely,

$$C_6H_4{<}\begin{matrix}CO{\cdot}NH{\cdot}CH_2\\ \qquad\quad | \\ CO{-}O{-}CH_2\end{matrix},HCl,H_2O.$$

It begins to sinter at 87° and melts at 91—92°. The *base* crystallises from alcohol, melts at 139°, and is readily soluble in acids and alkalis. The *aurichloride* softens at 155° and melts at 169—171°; the *platinichloride* crystallises in compact, golden-yellow prisms, turns yellow at 187°, and then darkens and decomposes. When distilled under reduced pressure the imino-base is converted into β-hydroxyethylphthalimide and, when evaporated with hydrobromic acid, into β-bromoethylphthalimide. With aqueous potassium hydroxide, it yields a *potassium* salt, $C_6H_4{<}\begin{matrix}CO{\cdot}NK{\cdot}CH_2\\ \qquad\quad | \\ CO{-}O{-}CH_2\end{matrix}$, which is sparingly soluble in excess of the alkali. When the potassium salt is heated with benzyl chloride and then hydrolysed with fuming hydrobromic acid, β-bromoethylbenzylamine is formed. When heated for a short time with water, the base is converted into *β-aminoethyl hydrogen phthalate*, $CO_2H{\cdot}C_6H_4{\cdot}CO_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$, which melts and decomposes at 149—150°. The *hydrochloride*, $C_{10}H_{11}O_4N,HCl$, melts and decomposes at 189° and the *platinichloride* at about 220°. The *hydrochloride* of the *methyl* ester, $CO_2Me{\cdot}C_6H_4{\cdot}CO_2{\cdot}C_2H_4{\cdot}NH_2,HCl$, crystallises in six-sided plates and melts at 130—131°; the ester itself is an oil.

J. J. S.

Nitroso-derivatives of Oxygenated Imino-compounds. SIEGMUND GABRIEL (*Ber.*, 1905, **38**, 2405—2413).—The *nitrosoamine* of anhydro-γ-hydroxypropylphthalamic acid (preceding abstract),

$$C_6H_4{<}\begin{matrix}CO{\cdot}N(NO){\cdot}CH_2\\ {-}CO{\cdot}O{\cdot}CH_2{-}\end{matrix}{>}CH_2,$$

separates from boiling alcohol in crystals resembling gypsum; it melts and decomposes at 123°, is soluble in most organic solvents, and is decomposed when heated with hydrochloric acid or boiled for some time with alcohol. When warmed with a dilute potassium hydroxide solution, it yields nitrogen, phthalic acid, and trimethyleneglycol.

The *nitrosoamine*, $C_6H_4<\begin{matrix}CO\cdot N(NO)\\CO\cdot O\cdot CH_2\end{matrix}>CH_2$, obtained from β-bromoethylphthalimide, crystallises in pale yellow plates and melts and decomposes at 137°. When warmed with dilute alkali, it yields phthalic acid, acetylene, and nitrogen.

The *nitrosoamine*, $C_6H_4<\begin{matrix}CO\cdot N(NO)-\\CO\cdot O\cdot CHMe\end{matrix}>CH_2$, obtained from β-bromopropylphthalimide, crystallises in four-sided prisms and melts at 147—148°. When warmed with dilute sodium hydroxide, it yields phthalic acid, allylene, and nitrogen.

The *nitrosoamine*, $CO<\begin{matrix}N(NO)\\O\cdot CH_2\end{matrix}>CH_2$, obtained from hydroxyethylcarbamic anhydride (Gabriel and Eschenbach, Abstr., 1898, i, 62), crystallises from a mixture of ethyl acetate and light petroleum in long, silky needles melting at 53°, and readily soluble in most organic solvents. It is somewhat unstable and readily decomposes on exposure to the air, leaving a soft, resinous substance; when dissolved in dilute sodium hydroxide, it yields nitrogen and acetylene, but the amount of acetylene does not correspond with the equation $C_3H_4O_3N_2 = CO_2 + H_2O + N_2 + C_2H_2$.

Benzamidoethyl benzoate, $CO_2Ph\cdot CH_2\cdot CH_2\cdot NH\cdot COPh$, obtained by benzoylating aminoethyl benzoate (Gabriel and Heymann, Abstr., 1890, 1267), crystallises from ether in flat needles melting at 88—89°. A nitrosoamine could not be prepared in benzene solution, probably owing to the absence of basic properties.

Pyrrolidone yields an oily *nitrosoamine*, $\begin{matrix}CH_2\cdot CO-\\ | \\ CH_2\cdot CH_2\end{matrix}>N\cdot NO$, which reacts with dilute sodium hydroxide, yielding nitrogen and γ-butyrolactone.

Ethyl bromoethyloxamate, $CO_2Et\cdot CO\cdot NH\cdot C_2H_4Br$, obtained from bromoethylamine hydrobromide, potassium hydroxide, and ethyl oxalate at 0°, crystallises from light petroleum in long, glistening needles and melts at 61°. It has not been found possible to convert it into a cyclic imine by the elimination of ethyl bromide. J. J. S.

Reduction of Derivatives of Dinitrodiphenylmethane. H. Duval (*Compt. rend.*, 1905, **141**, 198—201).—4 : 4′-Dicyanodiphenylmethane, formed from 4 : 4′-diaminodiphenylmethane, melts on Maquenne's block at 169°, and the corresponding dicarboxylic acid at 323° (m. p. 165° and 290° respectively, Schöpff, Abstr., 1894, i, 600). Nitration of the dicarboxylic acid in a mixture of nitric and sulphuric acids leads to the formation of *dinitrodiphenylmethane*-4 : 4′-*dicarboxylic acid*, which melts at 278°, is soluble in acetone, alcohol, boiling acetic acid, or nitrobenzene, and on treatment with hydrogen chloride in alcoholic solution yields *ethyl dinitrodiphenylmethane*-4 : 4′-*dicarboxylate*; this crystallises from alcohol and melts at 117°. *Ethyl diaminodiphenylmethane*-4 : 4′-*carboxylate*, formed by reduction of the dinitro-ester with zinc dust and ammonium chloride in boiling alcoholic solution, crystallises in needles, melts at 148°, is soluble in benzene, ether, acetone, or hot alcohol, and on hydrolysis with alcoholic potassium hydroxide yields *diaminodiphenylmethane*-4 : 4′-*dicarboxylic acid*, which

crystallises from alcohol, melts at 329°, and dissolves in aqueous alkali hydroxides or acids.

The reduction of 2 : 2′-dinitro-4 : 4′-diaminodiphenylmethane (Schnitzspahn, Abstr., 1902, i, 436) by means of zinc dust and ammonium chloride in alcoholic solution leads to the formation of 4 : 4′-*diamino-2 : 2′-azoxydiphenylmethane*, $NH_2\cdot C_6H_3<{}^{N_2O}_{CH_2}>C_6H_3\cdot NH_2$, which crystallises in yellow needles, melts at 272°, and when boiled with zinc dust in alcoholic potassium hydroxide solution yields 4 : 4′-*diamino-2 : 2′-azodiphenylmethane*, $NH_2\cdot C_6H_3<{}^{N_2}_{CH_2}>C_6H_3\cdot NH_2$, melting at 233°. G. Y.

Gradual Dissociation of Mellitic Acid. ANTONIO QUARTAROLI (*Gazzetta*, 1905, **35**, i, 470—477).—Towards indicators, mellitic acid behaves as either a tervalent or a sexavalent acid, which would indicate a considerable difference between K_3 and K_4. The magnitudes of the six dissociation constants, K_1, K_2, K_3, &c., of the acid and its uni-, bi-, ter-, &c., metallic salts have been determined by the inversion of sucrose method. Taking K_1 as 100, $K_2 = 40{\cdot}463$, $K_3 = 14{\cdot}315$, $K_4 = 2{\cdot}205$, $K_5 = 1{\cdot}490$, and $K_6 = 1{\cdot}039$. These numbers give the following ratios: $K_1/K_2 = 2{\cdot}47$; $K_2/K_3 = 2{\cdot}82$; $K_3/K_4 = 6{\cdot}49$; $K_4/K_5 = 1{\cdot}47$, $K_5/K_6 = 1{\cdot}43$, which constitute an exception to the general rule that the difference between two consecutive constants is greater the higher the value of the first of them; with K_4, K_5, and K_6 the behaviour conforms to this law.

These irregularities are probably due to the fact that successive saturation of the carboxyl groups by means of alkali takes place not in the order 1, 2, 3, &c., but in the order 1, 3, 5, 2, 4, 6. T. H. P.

Hydrazine Derivatives of *o*-Aminobenzaldehyde. CESARE RONCAGLIOLO (*Gazzetta*, 1905, **35**, i, 510—514).—By treating *o*-aminobenzaldehyde with monoacylhydrazines, the author has attempted, without success, to obtain compounds containing a seven-atom chain in addition to the benzene nucleus of the aldehyde.

o-*Aminobenzylideneacetylhydrazide*, $NH_2\cdot C_6H_4\cdot CH{:}N\cdot NHAc$, prepared by the interaction of acetylhydrazine and *o*-aminobenzaldehyde in molecular proportions, separates from water in small crystals melting at 170° and is readily soluble in alcohol or acetone.

Acetylaminobenzylideneacetylhydrazide, $NHAc\cdot C_6H_4\cdot CH{:}N\cdot NHAc$, obtained by the action of acetic anhydride on the preceding compound, is deposited from aqueous solution in transparent, colourless crystals melting at 195—196° and is readily soluble in alcohol.

o-*Aminobenzaldazine*, $NH_2\cdot C_6H_4\cdot CH{:}N\cdot N{:}CH\cdot C_6H_4\cdot NH_2$, prepared by the action of a hydrazine salt on an aqueous alcoholic solution of *o*-aminobenzaldehyde, crystallises from alcohol in small, yellow needles melting at 243°. The *diacetyl* derivative,

$$NHAc\cdot C_6H_4\cdot CH{:}N\cdot N{:}CH\cdot C_6H_4\cdot NHAc,$$

crystallises from alcohol in yellow needles melting at 285—288°.

T. H. P.

Conversion of Cinnamaldehyde into Cinnamyl Alcohol. PHILIPPE BARBIER and GEORGES LESER (*Bull. Soc. chim.*, 1905, [iii], **33**, 858—859).—Cinnamaldehyde itself cannot be reduced in acid, alkaline, or neutral solution, as it immediately polymerises, but its diacetyl derivative, when reduced with iron filings and acetic acid (80 per cent.), yields a product distilling at 120—160° under 14 mm. pressure. When this is hydrolysed with alcoholic sodium hydroxide, pure cinnamyl alcohol is obtained; it melts at 32° and boils at 142—145° under 14 mm. pressure. J. J. S.

Preparation of Cuminoin and Cuminil. HEINRICH BILTZ and CARL STELLBAUM (*Annalen*, 1905, **339**, 294—296).—In order to prepare cuminoin, the commercial cuminaldehyde is purified by means of the sodium hydrogen sulphite compound, and then condensed by boiling with an aqueous alcoholic solution of potassium cyanide. The cuminoin is oxidised to cuminil with chromic acid. K. J. P. O.

cyclo**Geraniolideneacetone.** FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 158075).—*cyclo*Geraniolenealdehyde (Abstr., 1903, i, 764) condenses with acetone in the presence of sodium ethoxide, alkali hydroxides, barium hydroxide or borax, with or without the addition of water or alcohol, to form cyclo*geraniolideneacetone*, $CMe_2<\substack{CH=\!=CH\\CH_2\cdot CHMe}>CH\cdot CH\!:\!CH\cdot COMe$, a colourless, viscid oil, which boils at 130—135° under 14 mm. pressure and has an odour of roses and violets. C. H. D.

Dinitrodiaminoanthraquinonedioxamic Acids. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 158076).—1 : 5- and 1 : 8-Diaminoanthraquinones react with oxalic acid at 100—150°, or at lower temperatures if the water is removed as formed, yielding dioxamic acids, $OH\cdot C_2O_2\cdot NH\cdot C_6H_3<\substack{CO\\CO}>C_6H_3\cdot NH\cdot C_2O_2\cdot OH$, which are almost insoluble in water, but form soluble, yellow alkali salts. Mono-oxamic acids, yielding red salts, are formed at lower temperatures.

Nitric and sulphuric acids convert the dioxamic acids more readily than other acyl derivatives of anthraquinone into dinitro-derivatives. 4 : 8-*Dinitroanthraquinone*-1 : 5-*dioxamic acid* is orange, and yields 4 : 8-dinitro-1 : 5-diaminoanthraquinone on hydrolysis with alkalis.

Sodium sulphide dissolves the dioxamic acids to green solutions, becoming blue when warmed, and depositing bronze crystals of *sodium tetra-aminoanthraquinonedioxamates* on cooling. C. H. D.

1-Hydroxyanthraquinone-5-sulphonic Acid. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 158413).—Anthraquinone and its sulphonic acids are only oxidised by sulphuric acid to polyhydroxyanthraquinones when highly fuming acid is employed at a low temperature. Acid containing less than 40 per cent. of anhydride at temperatures above 100° only yields sulpho-derivatives. It is found, however, that sulphuric acid with 25—30 per cent. anhydride oxidises anthraquinone-1-sulphonic acid completely at 150° to 1-*hydroxyanthra*-

quinone-5-sulphonic acid, yielding a yellow, crystalline sodium salt. Heating with milk of lime under pressure converts it into anthrarufin.

C. H. D.

[A New Aminodihydroxyanthraquinonesulphonic Acid.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 158150).—The purpurinsulphonic acid previously described (this vol., i, 146) reacts with ammonia rapidly at 120°, more slowly under atmospheric pressure, to form a new *aminohydroxyanthraquinonesulphonic acid*. The reaction is complete when a sample dissolved in sulphuric acid gives a strong yellow fluorescence with boric acid. The new acid dissolves in water to a reddish-violet solution, becoming violet with sodium carbonate, and in hot aniline to a red solution.

C. H. D.

Preparation of *o*-Dimethoxyanthraquinones. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 158278).—Nitromethoxyanthraquinones, in which the nitro- and methoxy-groups are attached to neighbouring carbon atoms, are converted by sodium hydroxide in methyl-alcoholic solution into dimethoxy-derivatives. Other isomerides, such as 4-nitro-1-methoxyanthraquinone, yield only a mixture of nitrohydroxy- and aminomethoxy-anthraquinone.

Alizarin dimethyl ether, from 1-nitro-2-methoxyanthraquinone, crystallises from alcohol in yellow needles and melts at 210°. It is not possible to prepare it by direct methylation of alizarin (Graebe and Aders, Abstr., 1902, i, 42). Heating with sulphuric acid converts it into the monomethyl ether.

Anthragallol trimethyl ether, from 1 : 3-dinitro-2-methoxyanthraquinone, crystallises from alcohol in light brown needles and melts at 160°.

C. H. D.

Methylcamphenylol. ST. MOYCHO and FR. ZIENKOWSKI (*Ber.*, 1905, **38**, 2461—2464. Compare Wagner, Moycho, and Zienkowski, Abstr., 1904, i, 438; Bouveault and Blanc, this vol., i, 222).—The oxidation product, formed by the action of chromic acid in concentrated aqueous solution on methylcamphenylol dissolved in glacial acetic acid, yields a mixture of camphor semicarbazone and a semicarbazone which melts at 215—216° and yields a ketone or mixture of ketones melting at 113—115°.

The camphene formed by dehydration of methylcamphenylol by means of 30 per cent. sulphuric acid boils at 157—158°, and on oxidation with potassium permanganate yields camphenylone, camphenylic acid, and a small proportion of camphenecamphoric acid; with glacial acetic acid and sulphuric acid, it yields *iso*bornyl acetate, which completes the cyclic process:

$$\begin{tikzcd} & \text{camphene} \arrow[r] & \text{camphenylone} \arrow[d] \\ \textit{iso}\text{borneol} \arrow[ur] & & \\ & \text{camphene} \arrow[ul] & \text{methylcamphenylol.} \arrow[l] \end{tikzcd}$$

G. Y.

Cyclene Bromide (Solid Pinene Bromide). J. O. GODLEWSKY (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 424—438. Compare Abstr., 1899, i, 618 and 920).—The action, at the ordinary temperature, of

silver acetate on solid pinene bromide in acetic acid solution and in absence of light yields sobrerol and the corresponding acetic ester. If the mixture is kept for a long time and is then gradually heated to 100°, it yields pinol, the acetic esters of carveol and sobrerol, and sobrerol itself. The author considers that only sobrerol and its acetic ester are formed directly from the pinene bromide, the other compounds arising from these initial products when the conditions happen to be favourable to such changes. T. H. P.

Reactions of Guaiacum Resin. Paul Petit and Mayer (*Compt. rend.*, 1905, **141**, 193—195).—In an atmosphere of hydrogen, tincture of guaiacum gives a blue coloration with solutions of ferric or manganic salts containing 0·02 milligram of metal per 100 c.c.; the ferric chloride is gradually reduced to ferrous chloride as shown by the disappearance of the blue colour, the formation of a blue coloration with potassium ferricyanide, and the reappearance of the original blue on addition of hydrogen peroxide. With silver nitrate or carbonate, guaiacum gives a blue coloration, with formation of silver oxide and metallic silver and quantitative liberation of the acid.

Guaiacum gives no blue coloration with ferrous chloride in an atmosphere of hydrogen, but does so immediately on admission of the least trace of air, similarly manganous acetate or lactate, but not the chloride, gives the coloration in contact with air.

In an atmosphere of hydrogen, guaiacum tincture dissolves (*a*) ferrous oxide to form a colourless solution which becomes blue on exposure to the air, or on addition of hydrogen peroxide; (*b*) manganous oxide to a colourless solution which becomes blue on contact with air only in presence of traces of acetic or lactic acid; and (*c*) manganic oxide to a green solution becoming blue on contact with air in presence of traces of an acid, or on addition of hydrogen peroxide.

With ferric oxide, guaiacum forms a compound which is insoluble in water, but soluble in alcohol. The blue colouring matters formed by guaiacum with ferric, manganic, or silver salts dissolve in chloroform or alcohol, or less readily in benzene, to solutions which rapidly decolorise.

In presence of albumin, the sensitiveness of the guaiacum reaction is greatly diminished; this effect is partially neutralised by the presence of an excess of acid. G. Y.

Gentiopicrin. Georges Tanret (*Compt. rend.*, 1905, **141**, 207—209. Compare Bourquelot and Hérissey, Abstr., 1900, i, 511).—The alcoholic extract of fresh gentian is diluted to 17 per cent. with water, extracted with hot ethyl acetate, and the syrup obtained on evaporation of the extract dried and recrystallised from boiling absolute alcohol. Owing to the presence of about 1 per cent. of gentiin the product gives a coloration with ferric chloride, and must be further purified by recrystallisation from hot ethyl acetate containing 2 per cent. of water, the gentiin accumulating in the mother liquors, which are evaporated finally to dryness, the residue being recrystallised from water and again treated with ethyl acetate. A yield of 70—140 grams of gentiopicrin is obtained in this manner from 1 kilogram of dried alcoholic extract.

Gentiopicrin $C_{16}H_{20}O_9,\frac{1}{2}H_2O$, forms orthorhombic crystals, melts at 122° ($2C_{20}H_{30}O_{12},1\frac{1}{2}H_2O$, m. p. 120—125°; Kromayer, *Arch. Pharm.*, **110**, 25), or when anhydrous at 191°, has $[\alpha]_D - 198{\cdot}75°$, and is hydrolysed by emulsin to dextrose and gentiogenin. When neutralised with potassium hydroxide or baryta, gentiopicrin forms the salts $C_{16}H_{21}O_{10}K$ and $(C_{16}H_{21}O_{10})_2Ba$ respectively, and when heated with acetic anhydride and zinc chloride it yields a *penta-acetyl* derivative, $C_{16}H_{15}O_4(OAc)_5$, which melts at 139° and has $[\alpha]_D - 164°$. G. Y.

Myristicin. II. ENRICO RIMINI (*Gazzetta*, 1905, **35**, i, 406—416. Compare this vol., i, 198).—The action of nitrous acid on *iso*myristicin yields (1) iso*myristicin nitrosite*, $C_{11}H_{12}O_6N_2$, which separates in yellowish-white clots, melting and decomposing at 130—131°; (2) iso*myristicin nitrosate*, $C_{11}H_{12}O_7N_2$, which crystallises from ether in orange-yellow plates, melting and decomposing slightly at 147°.

*β-Nitro*iso*myristicin*, $OMe{\cdot}C_6H_2(CH_2O_2){\cdot}CH{:}CMe{\cdot}NO_2$, obtained by boiling *iso*myristicin nitrosite, suspended in alcohol, with piperidine, crystallises from alcohol in golden-yellow, long, silky needles melting at 112°. On boiling its alcoholic solution with hydroxylamine hydrochloride and alkali, it yields *myristicin aldoxime*, $C_9H_9O_4N$, which crystallises from alcohol in minute needles, melting at 158°. *Dibromo-β-nitro*iso*myristicin*, $OMe{\cdot}C_6Br_2(CH_2O_2){\cdot}CH{:}CMe{\cdot}NO_2$, crystallises from alcohol in yellowish-white plates melting at 160°; with hydroxylamine, it yields nitroethane and *dibromomyristicin aldoxime*, $C_9H_7O_4NBr_2$, which softens at about 180° and melts at 184—186°.

When di*iso*nitroso*iso*myristicin (*loc. cit.*) is boiled with 20 per cent. sulphuric acid solution, it yields iso*myristicin diketone monoxime*, $C_{11}H_{11}O_5N$, which crystallises from benzene in mammillary masses melting at 154°. If to the action of 20 per cent. sulphuric acid is added that of a current of steam, di*iso*nitroso*iso*myristicin yields iso*myristicin diketone*, $C_{10}H_{10}O_3$, which crystallises from water in long, lemon-yellow needles melting at 45°, is readily soluble in alcohol, and gives a *disemicarbazone*, forming a heavy, white powder melting and decomposing at 235—236°.

On heating the above diketone monoxime with acetic anhydride and neutralising the product with sodium carbonate, it gives *myristicyldiacetylamide*, $OMe{\cdot}C_6H_2(CH_2O_2){\cdot}CO{\cdot}NAc_2$, which separates from alcohol in minute, whitish-yellow needles melting at 143°, and is decomposed by sodium hydroxide solution, yielding ammonia and myristicinic and acetic acids. T. H. P.

Dimroth's Thiophen Dimercuric Hydroxyacetate. CARL SCHWALBE (*Ber.*, 1905, **38**, 2208—2210. Compare Dimroth, Abstr., 1899, i, 428).—The compound described by Dimroth as thiophen dimercuric hydroxyacetate contains much less sulphur than would correspond with the formula attributed to it; its formation cannot be used as an accurate means of estimating thiophen in benzene as results are obtained far in excess of the actual amount. It is probably not a definite substance, but a mixture. W. A. D.

Aconitine. II. HEINRICH SCHULZE (*Chem. Centr.*, 1905, i, 1709; from *Apoth.-Zeit.*, **20**, 368—369).—Aconine, obtained from the hydro-

chloride by means of sodium carbonate, forms an almost colourless, resinous mass, or a loose, white, rather hygroscopic powder. The temperature at which it melts varies very much with the speed at which it is heated. The *hydrobromide*, $C_{25}H_{42}O_9N,HBr,1\frac{1}{2}H_2O$ or

$C_{25}H_{40}O_9N,HBr,1\frac{1}{2}H_2O$,

forms rather large, lustrous crystals. The nitrate and sulphate have not been obtained in a crystalline form, and attempts to prepare a nitrosoamine failed. Aconine does not react with hydroxylamine, formaldehyde, or phenylhydrazine; phenylcarbimide yields an amorphous product, which is not homogeneous. The alkaloid contains four methoxy-groups and a methyl group which is combined with nitrogen; the latter can be split off by Herzig and Meyer's method. Attempts to prepare a methyl derivative by means of methyl iodide or sulphate failed; a phenol-hydroxyl group does not appear to be contained in the molecule. *Tetra-acetylaconine*, $C_{33}H_{40}O_{13}N$ or $C_{33}H_{47}O_{13}N$, crystallises from alcohol in white needles and melts and decomposes at 230—231°. *Triacetylaconitine*, $C_{40}H_{53}O_{14}N$ or $C_{40}H_{51}O_{14}N$, crystallises from alcohol in white needles, combined together in spherical aggregates, and melts at 207—208°; the *aurichloride* forms an amorphous, canary-yellow precipitate and sinters at 140—145° without showing a definite melting point. The behaviour of aconitine towards methyl sulphate shows that the molecule not only contains two hydroxyl groups, of which the hydrogen may be replaced by an acetyl or benzoyl group, but also three more hydroxyl groups, which are probably of an alcoholic nature. Since aconine is not attacked by potassium permanganate in Willstätter's test, the molecule does not appear to contain double linkings. E. W. W.

α-Methyltetrahydroberberine. MARTIN FREUND and FRITZ MAYER (*Ber.*, 1905, **38**, 2652—2654).—*α-Methyltetrahydroberberine*, $C_{21}H_{23}O_4N$, prepared by the electrolytic reduction in a Tafel leaden beaker (Abstr., 1900, ii, 588) of α-methyldihydroberberine (this vol., i, 151) in aqueous alcoholic sulphuric acid, crystallises from alcohol in faintly coloured plates melting at 166—167° with previous softening. This compound is structurally analogous with corydaline, and as the molecule contains two asymmetric carbon atoms, it should exist in two isomerides each consisting of a pair of enantiomorphs. T. H. P.

Alkaloid Salts of Methylarsonic Acid (Arrhenalic Acid). DIOSCORIDE VITALI (*Chem. Centr.*, 1905, i, 1699—1701; from *Boll. Chim. Farm.*, **44**, 229—237, 265—273).—The methylarsonates (arrhenalates) are prepared by mixing solutions of the alkaloid sulphate (1 mol.) with disodium methylarsonate (rather more than 1 mol.) and a small quantity of water, evaporating to dryness, and extracting the finely powdered residue with boiling absolute alcohol. The salts separate on cooling or on evaporating the solution.

Anhydrous *quinine methylarsonate*, $(C_{20}H_{24}O_2N_2)_2AsO(OH)_2Me$, forms colourless, odourless crystals and has a very bitter taste; it melts and turns yellow at 139—141° and at a higher temperature becomes black and emits nauseous yellow fumes. One part of the salt is soluble in 2000 of water at 20°, in about 30 of absolute alcohol,

55 of 90 per cent. alcohol, 25 of methyl alcohol, 1000 of glycerol, 500 of acetone, or 1000 of chloroform. It is more soluble in boiling water than in cold and is practically insoluble in benzene, light petroleum, or toluene, but dissolves in acids.

Quinine hydrogen methylarsonate, $C_{20}H_{24}O_2N_2,AsO(OH)_2Me$, forms colourless, odourless crystals and has a very bitter taste; it melts and becomes brown at 151—154° and at higher temperatures turns black and emits red vapour, which condenses to a red oil. One part dissolves in 600 of water at 19°, in about 30 of absolute alcohol, 40 of 90 per cent. alcohol, 140 of amyl alcohol, 300 of ethyl acetate, 10 of methyl alcohol, or 300 of acetone. It is almost insoluble in ether or light petroleum but dissolves in dilute acids. The aqueous solution has a faint acid reaction.

Strychnine methylarsonate, $(C_{21}H_{22}O_2N_2)_2{\cdot}AsO(OH)_2Me$, forms a colourless, odourless, crystalline mass and has a bitter taste. One part dissolves in 1000 of water, in about 200 of alcohol, 500 of glycerol, or 400 of amyl alcohol; it is sparingly soluble in ethyl acetate, light petroleum, or benzene, but dissolves in dilute acids. The aqueous solution is neutral.

Strychnine hydrogen methylarsonate, $C_{21}H_{22}O_2N_2{\cdot}AsO(OH)_2Me$, forms colourless, odourless crystals and has a bitter taste. One part dissolves in about 600 of water, 180 of 95 per cent. alcohol, 156 of amyl alcohol, 200 of glycerol, or 1225 of acetone. It is readily soluble in acids, but only very sparingly so in ethyl acetate and almost insoluble in ether, light petroleum, or chloroform.

A table is given showing the precipitates formed by adding solutions of the salts of some eighteen alkaloids to a 1 per cent. solution of disodium methylarsonate. E. W. W.

Stable Quaternary Salts of Apomorphine. Robert Pschorr (D.R.-P. 158620).—The quaternary salts of apomorphine, with the exception of the methiodide, are more stable and more readily crystallised than the hydrochloride hitherto employed. These salts may be prepared from apomorphine methiodide and the corresponding silver salt, or by decomposing the methiodide with moist silver oxide and adding the corresponding acid to the solution of the base thus obtained.

Apomorphine methochloride crystallises from alcohol in colourless, glistening prisms, melts at 205—210°, and dissolves readily in water or alcohol, but is insoluble in ether. The *methobromide* separates from methyl alcohol and acetone in colourless scales or six-sided plates, containing 1 mol. of acetone, and melts when dry at 180°. The methonitrate, from apomorphine and methyl nitrate, crystallises from alcohol and acetone in colourless leaflets and dissolves readily in water or alcohol (compare Abstr., 1903, i, 512). C. H. D.

Pilocarpine and its Transformation into a New Modification. Adolf Pinner (*Ber.*, 1905, **38**, 2560—2561).—When pilocarpine hydrochloride is heated at 225—235° for 1—2 hours, then dissolved in a little water and a 50 per cent. solution of potassium carbonate added, the oily base which separates is only partially soluble in chloroform.

The portion which is insoluble in chloroform is a new modification of pilocarpine, designated by the author as *metapilocarpine.* It differs from pilocarpine and *iso*pilocarpine with respect to its salts, which are more soluble than those of its isomerides. Its *platinichloride* decomposes at 200°. By the action of strong bases on metapilocarpine or its alkyl derivative, only one nitrogen atom is eliminated as methylamine, whilst acids containing nitrogen are formed. Metapilocarpine has the formula $C_{11}H_{18}O_3N_2$. Its *hydrochloride, methiodide,* and *ethobromide* were prepared. A. McK.

Symmetry of the Sparteine Molecule. Charles Moureu and Amand Valeur (*Compt. rend.,* 1905, **141**, 117—119. Compare this vol., i, 608, 609).—Contrary to Scholtz and Pawlicki's statements (Abstr., 1904, i, 1045), the nitrogen atoms of sparteine have the same function, and must therefore be situated symmetrically in the molecule, as the products obtained on adding either methyl iodide and hydriodic acid, or reversely hydriodic acid and methyl iodide, are identical, as are also the hydriodides of sparteine formed by addition of hydriodic acid to the free base or by elimination of methyl iodide from the hydriodide of sparteine methiodide.

The authors find that ethyl iodide does not react with sparteine methiodide at 150°, but that at 200—205° ethylene and sparteine dihydriodide are formed. Sparteine ethiodide does not enter into reaction with methyl iodide at 140°. G. Y.

Dichloropyrrole and Dichlorodibromopyrrole. IX. Girolamo Mazzara and Alessandro Borgo (*Gazzetta,* 1905, **35**, i, 477—486. Compare Abstr., 1904, i, 614, 770, 771, 918, and 919).—The authors give new methods for preparing 2 : 5-dichloropyrrole and 2 : 5-dichloro-3 : 4-dibromopyrrole.

2 : 5-*Dichloro*-3 : 4-*dibromo*-1-*methylpyrrole,* $NMe<\begin{matrix}CCl:CBr\\ |\\ CCl:CBr\end{matrix}$, prepared by the action of methyl-alcoholic potassium hydroxide and methyl iodide on a solution of 2 : 5-dichloro-3 : 4-dibromopyrrole in methyl alcohol, crystallises from alcohol in long, white needles melting at 126° and is readily soluble in light petroleum. When oxidised with concentrated nitric acid of sp. gr. 1·48, it yields dibromomaleinmethylimide.

When chlorine enters the pyrrole molecule, it first replaces the hydrogen in the 2- and 5-positions, then that in the 3- and 4-positions, and finally the iminic hydrogen. T. H. P.

Transformations of the Nitrosopyrroles. Francesco Angelico (*Atti Real. Accad. Lincei,* 1905, [v], **14**, i, 699—703).—The action of hydroxylamine on an alkaline solution of *iso*nitrosopyrrole yields an *anhydro-trioxime,* $C_4H_5O_2N_3$, which crystallises from water in shining, white needles melting and decomposing at 248—250°. The formation of this compound shows that the *iso*nitroso-group of *iso*nitrosopyrrole must be in the 3-position, since if it were in the 2-position a dioxime should be produced.

Similarly, 3-nitrosophenylmethylpyrrole and hydroxylamine yield the *trioxime,* NOH:CPh·C(NOH)·CH_2·CMe:NOH or

NOH:CPh·CH_2·C(NOH)·CMe:NOH,

which crystallises from alcohol in minute, white needles melting and decomposing at 205°, and behaves towards reagents in a manner quite analogous with that of the trioxime from nitrosodimethylpyrrole (Angelico and Calvello, Abstr., 1904, i, 447). It gives a *tribenzoyl* derivative, $C_{32}H_{25}O_6N_3$, which separates from alcohol in minute crystals melting at 156°. When heated for a short time with dilute sulphuric acid, it loses hydroxylamine, giving rise to a *compound*, $C_{11}H_{10}O_2N_2$, which crystallises from benzene in faintly yellow plates, melts at 170°, dissolves in alkalis, and forms a *benzoyl* derivative, $C_{18}H_{14}O_3N_2$, separating from alcohol in minute, white crystals melting at 158—159°. When subjected to the prolonged action of dilute sulphuric acid, the trioxime loses all its hydroxylamine, giving a *ketone*, $C_{11}H_9O_2N$, which crystallises from alcohol in white leaflets melting at 105° and yields a *hydrazone*, $C_{17}H_{14}O_3N_4$, crystallising from alcohol in minute, intensely yellow needles melting and decomposing at about 200°.

On heating the trioxime for a long time with water, it loses $1H_2O$, giving a *compound*, $C_{11}H_{11}O_2N_3$, which is deposited from light petroleum in small, prismatic crystals melting at 88°. Treatment of this compound with dilute sulphuric acid gives rise to a *ketone*, $C_{11}H_{10}O_2N_2$, which crystallises from light petroleum in long, white needles melting at 95°, and yields a p-*nitrophenylhydrazone*, $C_{17}H_{15}O_3N_5$, crystallising from alcohol in intensely yellow, slender needles melting and decomposing at about 202°.

3-Nitrosodiphenylpyrrole and hydroxylamine yield (1) an *anhydrotrioxime*, $C_{16}H_{13}O_2N_3$, which separates from benzene in pale yellow, rhombic crystals melting at 141—142°; its *benzoyl* derivative, $C_{23}H_{17}O_3N_3$, separates from light petroleum in minute, white crystals melting at 123°: (2) small quantities of two very characteristic compounds which are insoluble in alkalis. One of these is readily soluble in alcohol, from which it is deposited in red crystals; the other and less soluble one is yellow, but when rubbed or when boiled for a long time with alcohol it becomes converted into the red compound and passes into solution.

3-*Aminotriphenylpyrrole*, $C_{22}H_{18}N_2$, prepared by reducing 3-nitrosotriphenylpyrrole with either hydroxylamine or zinc dust and acetic acid, crystallises from benzene in slender, white needles melting at 184—185°. Its *benzoyl* derivative, $C_{29}H_{22}ON_2$, separates from benzene in minute crystals melting and decomposing at 123°. Treatment with potassium cyanate yields the corresponding *carbamide*, $C_{23}H_{19}ON_3$, which is deposited from alcohol in crystals melting and decomposing at 238°.

These results show that the introduction of phenyl groups retards or prevents the hydrolysis of the pyrrole ring, whilst the presence of the *iso*nitroso-group favours the breaking of the ring. T. H. P.

Condensation Products of Semicarbazide and Ethyl Diacetylsuccinate. Carl Bülow, Gustav Riess, and Constantin Sautermeister (*Ber.*, 1905, **38**, 2366—2375. Compare Abstr., 1903, i, 196; Borsche and Spannagel, Abstr., 1904, i, 779).—Ethyl diacetylsuccinate readily condenses with semicarbazide hydrochloride in the

presence of sodium acetate and acetic acid, yielding *ethyl* 1-*carbamido*-2 : 5-*dimethylpyrrole*-3 : 4-*dicarboxylate*,

$$NH_2\cdot CO\cdot NH\cdot N<\begin{matrix}CMe:C\cdot CO_2Et\\ | \\ CMe:C\cdot CO_2Et\end{matrix},$$

which crystallises from dilute alcohol in slender needles, melts at 202—203°, and dissolves readily in hot acetone, alcohol, or glacial acetic acid. It dissolves also in alkalis owing to the acidic properties of the imino-hydrogen atom. When hydrolysed with 15 per cent. aqueous potassium hydroxide, the ester yields the corresponding *acid*, $C_9H_{11}O_5N_3$, which crystallises from hot alcohol in microscopic needles melting at 241° and is practically insoluble in benzene, chloroform, or light petroleum. Its ammonium salt yields precipitates with solutions of silver, mercurous, mercuric, plumbous, and stannous salts. When fused at 175° with solid potassium hydroxide, the ester is converted into 1-*amino*-2 : 5-*dimethylpyrrole*-3 : 4-*dicarboxylic acid*,

$$NH_2\cdot N<\begin{matrix}CMe:C\cdot CO_2H\\ | \\ CMe:C\cdot CO_2H\end{matrix},$$

which crystallises from alcohol in nodular masses, melts and decomposes at 210°, and dissolves in alcohol, acetic acid, hot water, or alkalis.

When methylated with methyl sulphate in the presence of potassium hydroxide, the ester yields *ethyl* 1-*methylcarbamido*-2 : 5-*dimethylpyrrole*-3 : 4-*dicarboxylate*, $NH_2\cdot CO\cdot NMe\cdot N<\begin{matrix}CMe:C\cdot CO_2Et\\ | \\ CMe:C\cdot CO_2Et\end{matrix}$, which crystallises from water in glistening plates melting at 151°. When hydrolysed with 10 per cent. potassium hydroxide, the methylated ester yields the corresponding *acid*, $C_{10}H_{13}O_5N_3$, which melts and decomposes at 263°. When fused with solid potassium hydroxide at 170°, it yields alcohol, ammonia, carbon dioxide, and 1-*methylamino*-2 : 5-*dimethylpyrrole*-3 : 4-*dicarboxylic acid*,

$$NHMe\cdot N<\begin{matrix}CMe:C\cdot CO_2H\\ | \\ CMe:C\cdot CO_2H\end{matrix},$$

melting at 182—183°.

The ester of the carbamido-acid, when benzoylated by the Schotten-Baumann method, yields Bülow's ethyl 1-dibenzoylamino-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate, melting at 132°, and the corresponding monobenzoyl derivative, melting at 123—124°. J. J. S.

Condensation of Nitromethane with Alkyl Derivatives of Aminomethyl Alcohol. Louis Henry (*Bull. Acad. roy. Belg.*, 1905, 214—230).—As the result of a correction by Düden and the subsequent determination of the molecular weights of some of his compounds, the author acknowledges that nitromethane condenses only with two molecules of piperidylcarbinol, $C_5NH_{10}\cdot CH_2\cdot OH$, and not with three, as previously stated by him (*ibid.*, 1896, [iii], 32, 33).

Formaldehyde condenses in aqueous alcoholic solution with one molecule of the compound $NO_2\cdot CH(CH_2\cdot C_5NH_{10})_2$, giving rise to the substance $NO_2\cdot C(CH_2\cdot C_5NH_{10})_2\cdot CH_2\cdot OH$, which crystallises from benzene in needles melting at 101—102°; this substance may also

be obtained by the action of piperidine in aqueous solution on α-nitro-*tert.*-butanetriol, $NO_2\cdot C(CH_2\cdot OH)_3$. When boiled for a quarter of an hour with more piperidine, the first compound is converted into a stereoisomeric modification, which crystallises from alcohol in small needles melting at 78—79°. P. H.

Action of Formaldehyde on 1 : 2-Dimethyl-Δ^2-tetrahydropyridine. II. 3-Acetyl-1-methylpiperidine (1-Methyl-3-piperyl Methyl Ketone). ANDREAS LIPP and EDUARD WIDNMANN (*Ber.*, 1905, **38**, 2471—2482. Compare this vol., i, 610).—The formation of 1-methyl-3-ethylpiperidine by the action of formaldehyde on 1 : 2-dimethyl-Δ^2-tetrahydropyridine and reduction of the product is explained by the hydrolysis of 1 : 2-dimethyl-Δ^2-tetrahydropyridine,

$$CH_2<\begin{matrix}CH:CMe\\CH_2\cdot CH_2\end{matrix}>N\cdot Me,$$

in aqueous solution to methyl methylaminobutyl ketone,

$$NHMe\cdot[CH_2]_4\cdot COMe$$

(compare Lipp, Abstr., 1896, i, 317). With formaldehyde, this forms a methylol derivative, $NHMe\cdot[CH_2]_3\cdot CH(COMe)\cdot CH_2\cdot OH$, which condenses to 3-acetyl-1-methylpiperidine,

$$CH_2<\begin{matrix}CH(COMe)\cdot CH_2\\CH_2\text{———————}CH_2\end{matrix}>NMe.$$

Methyl benzoylmethylaminobutyl ketone, $COMe\cdot[CH_2]_4\cdot NMeBz$, is formed by the action of benzoyl chloride on 1 : 2-dimethyl-Δ^2-tetrahydropyridine in aqueous sodium hydroxide solution. It is a colourless, viscid oil, which is not solid at −12°, is soluble in alcohol or ether, but only slightly so in water, forming an alkaline solution, and is not decomposed by evaporation with hydrochloric acid or heating with fuming hydrochloric acid at 100°; it yields benzoic acid and 1 : 3-dimethyl-Δ^2-tetrahydropyridine hydrochloride when heated with fuming hydrochloric acid in a sealed tube at 140—150°. When warmed with hydroxylamine hydrochloride and sodium carbonate in aqueous alcoholic solution, the benzoyl compound forms an *oxime*, which is obtained as a yellow oil soluble in aqueous potassium hydroxide. The phenylhydrazone of the benzoyl compound could not be purified.

The *hydrochloride* of methyl methylaminobutyl ketoxime, formed by warming 1 : 2-dimethyl-Δ^2-tetrahydropyridine with hydroxylamine hydrochloride in aqueous solution, is obtained on evaporation of its solution as a crystalline mass. The *oxime*, $OH\cdot N:CMe\cdot[CH_2]_4\cdot NHMe$, crystallises in rhombic plates, melts at 80—81°, is slightly hygroscopic, and dissolves in water to an alkaline solution. The aqueous solution of 1 : 2-dimethyl-Δ^2-tetrahydropyridine reacts with semicarbazide hydrochloride to form the *hydrochloride* of methyl methylaminobutyl ketone semicarbazone, $NH_2\cdot CO\cdot NH\cdot N:CMe\cdot[CH_2]_4\cdot NHMe,HCl$, which separates from alcohol in white, nodular, crystalline aggregates, melts and decomposes at 162°, has a slight acid reaction in aqueous solution, and reduces Fehling's solution when warmed. The *semicarbazone* crystallises in sheaves of needles and dissolves in water to an alkaline solution, which on warming evolves ammonia. 1 : 2-Dimethyl-Δ^2-tetra-

hydropyridine reacts with phenylhydrazine in aqueous solution to form an unstable hydrazone.

The *oxime* of 3-acetyl-1-methylpiperidine, $OH\cdot N\colon CMe\cdot C_5NH_9Me$, formed by the action of hydroxylamine hydrochloride and sodium carbonate on the hydrochloride of the condensation product of formaldehyde with 1 : 2-dimethyl-Δ^2-tetrahydropyridine, crystallises in small prisms, melts at 117—120°, and is soluble in aqueous potassium hydroxide. The *hydrochloride* of the phenylhydrazone,

$$NHPh\cdot N\colon CMe\cdot C_5NH_9Me,HCl,$$

forms glistening, granular crystals, melts and decomposes at 201—202°, and does not reduce boiling Fehling's solution; the *phenylhydrazone* is an oil. The *hydrochloride* of the semicarbazone,

$$NH_2\cdot CO\cdot NH\cdot N\colon CMe\cdot C_5NH_9Me,HCl,$$

crystallises in glistening plates containing $3H_2O$ and melts at 184° or, when anhydrous, with decomposition at 200—202°; the *semicarbazone* crystallises in nodular aggregates of glistening leaflets and melts at 175°.

The substance obtained by reduction of the condensation product with sodium amalgam and hydrochloric acid is 1-methyl-3-α-hydroxyethylpiperidine, $CH_2{<}{}^{CH_2-CH_2}_{NMe\cdot CH_2}{>}CH\cdot CHMe\cdot OH$, and not 1-methyl-2-β-hydroxyethylpiperidine as previously supposed (Abstr., 1897, i, 230); when oxidised with potassium dichromate in sulphuric acid solution, it yields 3-acetyl-1-methylpiperidine. G. Y.

Influence of Indifferent Solvents on the Alkylation of Organic Bases. NICOLAI MENSCHUTKIN (*Ber.*, 1905, **38**, 2465—2466. Compare Abstr., 1895, ii, 385; 1898, i, 119; 1900, i, 341; Pinner and Franz, this vol., i, 466).—A claim for priority.

G. Y.

Indole Colouring Matters. MARTIN FREUND and GUSTAV LEBACH (*Ber.*, 1905, **38**, 2640—2652. Compare Abstr., 1903, i, 278; 1904, i, 266).—Ehrlich found that an intensely red coloration is formed when hydrochloric acid is added to an alcoholic solution of 2-methylindole and dimethylaminobenzaldehyde. The authors find that this coloration is due to the formation of one of the rosindoles, the leuco-compounds of which are obtained by condensation of 1 mol. of an aldehyde with 2 mols. of indole or one of its derivatives with expulsion of water (compare Fischer and Wagner, Abstr., 1887, 588). For the condensation product obtained with 2-methylindole, the authors' results confirm the formula given by Fischer (Abstr., 1887, 265). It is found that in absolute alcoholic solution and in presence of hydrogen chloride, aldehydes also react in molecular proportions with 2-methylindole. The formation of the condensation products thus obtained, to which the name "*monoketoles*" is given, is explained by assuming that under these conditions 2-methylindole reacts not in the imino-form, but as indolenine. The condensation products will then be similar to the nitroso-derivatives studied by Spica and Angelico (Abstr., 1900, i, 938), and, like these, they have basic properties. Further confirmation of this constitution is furnished by the observation that condensation of 2-methylindole and an aldehyde in molecular

proportions does not take place when a substituent occupies the position of the hydrogen attached to the nitrogen of the indole, transformation into the indolenine form being then impossible.

On oxidation, the diketoles all yield red colouring matters. Similarly, oxidation of the monoketoles gives colouring matters which in this case almost all possess a blue tint. These compounds are obtained by digesting the monoketole in alcoholic or acetone solution with about half its weight of chloranil and a little alcoholic hydrogen chloride until no further change in colour occurs, the solution being then evaporated to dryness, and chloranil and its products of change removed from the residue by extraction with ether. The dyes are either insoluble or only very slightly soluble in water or dilute acids.

The authors suggest that the name "*indyl*" be given to the univalent indole residue, $\begin{array}{l} CH{:}CH\cdot C{-}{-}C{\lessgtr} \\ | \qquad\quad\;\, \| \\ CH{:}CH\cdot C\cdot NH \end{array}\!\!>CH$, and the name "*indolenylidene*" or "*indolidene*" to the bivalent complex, $\begin{array}{l} CH{:}CH\cdot C{-}C{=} \\ | \qquad\quad\;\, \| \\ CH{:}CH\cdot C\cdot N \end{array}\!\!\gg CH$, derived from indolenine. These terms are employed in the nomenclature of the following compounds.

p-*Dimethylaminophenyldi-2-methylindylmethane*,

$NMe_2\cdot C_6H_4\cdot CH(C_8NH_5Me)_2$,

prepared from dimethylaminobenzaldehyde and 2-methylindole, crystallises from a mixture of alcohol and acetone in white needles melting at 240—242°, and is soluble in benzene or chloroform and readily so in acetone or acetic acid. On oxidation, it yields a *dye*, which forms a brownish-violet powder and dissolves in hydrochloric acid to a red solution. The dye dissolves also in alcohol or acetone, the solution being decolorised by zinc dust and hydrochloric acid; the base separated by the addition of alkali gives a brown solution in alcohol. The *methiodide*, $NMe_3I\cdot C_6H_4\cdot CH(C_8NH_5Me)_2$, crystallises from aqueous alcohol in white needles melting at 181—182°. The colouring matter obtained from it dyes a reddish-violet colour.

p-*Dimethylaminophenyl-2-methylindolidenemethane*,

$NMe_2\cdot C_6H_4\cdot CH{:}C_8NH_4Me$,

obtained from dimethylaminobenzaldehyde and 2-methylindole, separates from a mixture of acetone and water as a brownish-violet, crystalline powder softening at 295° and melting at 305°, and is readily soluble in chloroform, benzene, or acetone. The dye obtained by oxidation is a dark brown powder with a metallic reflex and is readily soluble in alcohol, the solution being decolorised by zinc dust and acetic acid. The free base obtained by the action of alkali on the dye dissolves in alcohol, giving a brown solution.

o-*Chloro*-p-*dimethylaminophenyldi-α-methylindylmethane*,

$NMe_2\cdot C_6H_3Cl\cdot CH(C_8NH_5Me)_2$,

prepared from *o*-chloro-*p*-dimethylaminobenzaldehyde and 2-methylindole, crystallises from aqueous acetone in white needles melting at 236°. The colouring matter obtained by oxidising it dyes a reddish-violet colour.

o-*Chloro*-p-*dimethylaminophenyl-α-methylindolidenemethane*,

$NMe_2\cdot C_6H_3Cl\cdot CH{:}C_8NH_4Me$,

is a pale yellowish-brown substance, which sinters at 270° and melts at 282°. By means of chloranil, a bluish-violet dye is obtained.

o-*Chloro*-p-*dimethylaminophenyl-di-2-methyl-1-ethylindylmethane*,

$$NMe_2\cdot C_6H_3Cl\cdot CH(C_8NH_4MeEt)_2,$$

crystallises from a mixture of acetone and water in slender, white needles melting at 219°, and is slightly soluble in acetic acid or acetone, and readily so in chloroform or benzene.

The authors have been unable to prepare the monoketole, $CHPh\colon C_9NH_7$, but have separated the corresponding colouring matter as a bluish-black powder, which is soluble in alcohol giving a blue solution, and in aqueous alcoholic solution containing acetic acid dyes silk a greyish-blue colour.

o-*Chlorophenyldi-2-methylindylmethane*, $C_6H_4Cl\cdot CH(C_8NH_5Me)_2$, prepared from *o*-chlorobenzaldehyde and 2-methylindole, crystallises from alcohol in white needles sintering at 230° and melting at 240°. The colouring matter obtained from it by oxidation acts as a raspberry-red dye.

o-*Chlorophenyl-a-methylindolidenemethane*, $C_6H_4Cl\cdot CH\colon C_8NH_4Me$, crystallises from alcohol in pale brown scales having a golden lustre, and sinters at 185° and melts and decomposes at 194—195°.

o-*Nitrophenyldi-a-methylindylmethane*, $NO_2\cdot C_6H_4\cdot CH(C_8NH_5Me)_2$, crystallises from alcohol in pale yellow needles melting at 244°. The corresponding colouring matter is pale red with a violet tinge.

o-*Nitrophenyl-2-methylindolidenemethane*, $NO_2\cdot C_6H_4\cdot CH\colon C_8NH_4Me$, is pale brown, melts at 210° with previous sintering, and is soluble in ether or light petroleum. The *hydrochloride*, $C_{16}H_{12}O_2N_2,HCl$, separates from alcohol in pale brown crystals having a golden lustre and melting at 150°. The corresponding dye has a brown tone.

o-*Nitrophenyldi-2-methyl-1-ethylindylmethane* crystallises from aqueous acetone in pale yellow needles melting at 222—224°, and dissolves readily in chloroform, less readily in benzene or acetic acid, and slightly in alcohol or ether. It yields a bright reddish-violet dye.

p-*Nitrophenyldi-2-methylindylmethane*, $NO_2\cdot C_6H_4\cdot CH(C_8NH_5Me)_2$, separates from alcohol in yellow crystals melting at 238° and dissolves readily in acetone. The corresponding dye is reddish-violet.

m-*Hydroxyphenyldi-2-methylindylmethane*,

$$OH\cdot C_6H_4\cdot CH(C_8NH_5Me)_2,$$

forms crystals melting at 222° and is readily soluble in alcohol, ether, or acetone.

m-*Hydroxyphenyl-2-methylindolidenemethane*,

$$OH\cdot C_6H_4\cdot CH\colon C_8NH_4Me,$$

gives a *hydrochloride*, $C_{16}H_{14}ONCl$, which crystallises in yellowish-brown scales having a golden lustre, blackens at 160° and decomposes at 210—220°; it dissolves readily in alcohol and yields a brownish-violet dye.

o-*Hydroxyphenyldi-2-methylindylmethane*, $OH\cdot C_6H_4\cdot CH(C_8NH_5Me)_2$, prepared from salicylaldehyde and 2-methylindole, crystallises from alcohol in needles melting at 226° and dissolving readily in acetone, chloroform, or benzene. The dye obtained from it is yellowish-red.

o-*Hydroxyphenyl-2-methylindolidenemethane*, $OH\cdot C_6H_4\cdot CH\colon C_8NH_4Me$,

forms a yellowish powder melting at 185° and dissolving readily in alcohol. The *hydrochloride*, $C_{16}H_{13}ON,HCl$, crystallises from alcoholic hydrogen chloride in red leaflets with a golden lustre, and becomes brown at 190° and melts at 202°. The corresponding oxidation product is a violet-red dye.

o-*Hydroxyphenyldi-2-methyl-1-ethylindylmethane*,

$$OH\cdot C_6H_4\cdot CH(C_8NH_4MeEt)_2,$$

crystallises from a mixture of alcohol, acetone, and water in needles melting at 229°; the oxidation product dyes a red colour with a faint violet tinge.

3 : 4-*Methylenedioxyphenyldi-2-methylindylmethane*,

$$CH_2O_2\colon C_6H_3\cdot CH(C_8NH_5Me)_2,$$

prepared from piperonaldehyde and 2-methylindole, crystallises from alcoholic acetone in needles melting and decomposing at 206—212°, and dissolves readily in benzene or acetic acid. The colouring matter gives a red colour with a brown tinge.

3 : 4-*Methylenedioxyphenyl-2-methylindolidenemethane*,

$$CH_2O_2\colon C_6H_3\cdot CH\colon C_8NH_4Me,$$

gives a *hydrochloride* which separates from alcoholic hydrochloric acid in brown scales, darkening at 150° and decomposing at 194°, and readily soluble in acetone. The oxidation product dyes a brown colour with a violet tinge.

3 : 4-*Methylenedioxyphenyldi-2-methyl-1-ethylindylmethane*,

$$CH_2O_2\colon C_6H_3\cdot CH(C_8NH_4MeEt)_2,$$

crystallises from aqueous acetone in needles melting at 175°, and dissolves readily in chloroform or benzene. The oxidation product acts as a vivid brownish-red dye.

Diphenyl-α-methylindolidenemethane hydrochloride,

$$CPh_2\colon C_8NH_4Me,HCl,$$

crystallises from alcohol in brown needles melting at 205—206°, and dyes silk an intense brown colour. By the action of alkali, the base is obtained as an oil. T. H. P.

Action of Chloroform on 1 : 2 : 3-Trimethylindole. GIUSEPPE PLANCHER and ORESTE CARRASCO (*Atti R. Accad. Lincei*, 1905, [v], 14, i, 704—706. Compare Abstr., 1904, i, 777; and this vol., i, 298).—The action of chloroform on 1 : 2 : 3-trimethylindole in presence of sodium ethoxide yields 1 : 3-dimethyl-3-dichloromethyl-2-methyleneindoline, $C_6H_4{<}{\overset{CMe(CHCl_2)}{\underset{NMe}{}}}{>}C\colon CH_2$, the hydriodide of which is identical with the methiodide of 2 : 3-dimethyl-3-dichloromethylindolenine (*loc. cit.*). T. H. P.

Quinoline-2-carboxylic Chloride. HANS MEYER (*Ber.*, 1905, **38**, 2488—2490. Compare Abstr., 1901, i, 407; this vol., i, 155).—The melting points of pyridinecarboxylic and quinolinecarboxylic chlorides are approximately those of the hydrochlorides of the acids. These acid chlorides are insoluble in, or dissolve with decomposition in, organic solvents. The author has repeated the preparation of quinoline-2-carboxylic chloride, and finds it to melt and decompose between 168° and 175°, depending on the rate of heating; the amide

melts at 123° (Reissert, this vol., i, 472; m. p. 133°). No trace could be obtained of Besthorn and Ibele's substance melting at 97—98° (this vol., i, 612). G. Y.

Relationships of Doubly-linked Carbon to Nitrogen, Oxygen, and Sulphur. HERMANN DECKER (*Ber.*, 1905, 38, 2493—2511).—The transformation of substituted benzylidenedihydro*iso*quinolines into quaternary ammonium bases (Decker and Klauser, Abstr., 1904, i, 338) is a general one for analogous substances where the 2-position is occupied by an alkyl or benzyl group. In the change represented for 4-benzylpyridine by the equation

$$CHPh{:}C_5NH_4Me + H_2O \rightleftharpoons CH_2Ph{\cdot}C_5NH_4Me{\cdot}OH,$$

the benzyl group may be replaced by an alkyl group, the nitrogen atom attached to the methyl group by oxygen or sulphur, the pyridine ring by other rings, and the alkyl group may be substituted in the 2-position instead of in the 4-position. The alkylidene bases are yellow, whilst the hydroxides are colourless. The transformations indicated are interpreted in the light of Thiele's theory of partial valencies.

Since Fosse designates as "pyrylium" compounds those derivatives of pyrone where the oxygen atom acts as a tetravalent element, the author substitutes the term "xanthylium" for the term xanthonium, formerly employed by him. "Acridan" is also substituted for dihydroacridine, "quinolan" for dihydroquinoline, "pyridan" for dihydropyridine, &c. For the hydroxydihydro-bases, the terms "acridanol," "quinolanol," "pyridanol," &c., are introduced.

[With WASLAW WISLOCKI.]—The action of magnesium benzyl chloride on 1-methyl-2-pyridone is unsuitable as a method of formation of 2-benzylidenemethylpyridan. The latter was obtained, although not isolated, owing to its instability, from 2-benzylpyridine by Tschitschibabin's method. It is orange-coloured, and is readily acted on by water to form the colourless 2-benzyl-1-methylpyridinium hydroxide, from which it is readily regenerated by the action of sodium hydroxide.

[With OSKAR KLAUSER.]—The amount of *iso*papaverine which could be withdrawn from a solution of papaverine bromoethoxide by means of sodium hydroxide solutions of varying concentration was quantitatively determined. The transformation of ethyl*iso*papaverine into the corresponding quaternary ammonium base in benzene solution was also quantitatively studied.

The transformation of 2-benzylquinoline methiodide into the yellow benzylidenemethylquinolan and of benzylidenemethylacridan into the ammonium salt of 10-methylacridine was examined.

5-Methylacridine, prepared from diphenylamine and acetic acid, melts at 115° and boils at 359—360° under 740 mm. pressure; its *tertiary picrate* melts at 220—221°. Its quaternary salt was prepared by the action of methyl iodide or methyl sulphate; the *quaternary methyl picrate* melts and decomposes at 199°. 5-Methylacridine methiodide could not be converted into the corresponding carbinol base.

[With HANS BÜNZLY and THEODOR VON FELLENBERG.]—*Benzyl-*

xanthylium chloride, $C_{20}H_{15}OCl$, was obtained, in admixture with benzylidene base and carbinol, by the action of magnesium benzyl chloride on xanthone; its *ferrichloride*, $C_{20}H_{15}OCl,FeCl_3$, melts and decomposes at 148—150°; its *mercurichloride* melts at 144—146°. *Benzylxanthenol*, $O<\substack{C_6H_4\\C_6H_4}>C(CH_2Ph)\cdot OH$, prepared as one of the products of the foregoing Grignard reaction, separates from light petroleum in silky needles and melts at 132°. When benzylxanthylium salts are neutralised by alkalis, or when their solutions in acid are decomposed by water, 9-*benzylidenexanthen*,

$$O<\substack{C_6H_4\\C_6H_4}>C:CHPh,$$

is formed; it separates from alcohol in yellow needles and melts at 114—115°. 9-*Benzylxanthen*, $O<\substack{C_6H_4\\C_6H_4}>CH\cdot CH_2Ph$, prepared by the action of hydriodic acid on benzylxanthenol or benzylidenexanthen, forms glistening needles and melts at 71—72°.

When a mineral acid is added, at the ordinary temperature, to a colourless solution of benzylidenexanthen in acetic acid, the yellowish-red colour of the xanthylium salt appears.

The *tri-iodide*, $CMe\substack{\diagup C_6H_4 \diagdown\\ \diagdown C_6H_4 \diagup}OI:I_2$, prepared by the action of magnesium methyl iodide on xanthone, is a violet, crystalline mass. The *ferrichloride*, $C_{14}H_{11}OCl,FeCl_3$, melts at 240°; the *mercurichloride*, $C_{14}H_{11}OCl,HgCl_2$, melts at 189—190°. 9-*Methylxanthenol*, $C_{14}H_{12}O_2$, forms yellow needles and melts at 96—99°.

[With Theodor von Fellenberg.]—9-*Benzylthioxanthenol*, $C_{20}H_{16}OS$, prepared by the action of magnesium benzyl chloride on thioxanthone, crystallises in colourless needles and melts at 133°. On the addition of mineral acids, the red colour of the thioxanthylium salts is developed.

Benzylidenethioxanthen, $S<\substack{C_6H_4\\C_6H_4}>C:CHPh$, produced either as a by-product in the above Grignard reaction or by heating 9-benzylthioxanthenol, separates from light petroleum in almost colourless needles and melts at 114—115°. Coloured thioxanthylium salts are formed by the addition of mineral acids. The *ferrichloride*, $C_{20}H_{15}SCl,FeCl_3$, prepared by the addition of ferric chloride to a solution of a benzylthioxanthylium salt, softens at 135° and melts at 155°. The *mercurichloride*, $C_{20}H_{15}SCl,HgCl_2$, melts and decomposes at 148—149°.

Benzylthioxanthen, $S<\substack{C_6H_4\\C_6H_4}>CH\cdot CH_2Ph$, prepared by the action of hydriodic acid on a solution of 9-benzylthioxanthenol in acetic anhydride, separates from alcohol in glistening needles and melts at 127°.

The action between thioxanthone and magnesium methyl iodide leads to the formation of a thioxanthylium compound, the *mercurichloride*, $C_{14}H_{11}SCl,HgCl_2$, of which melts at 156—160°.

Methylthioxanthenol methyl ether, $C_{15}H_{14}OS$, forms hexagonal plates, and melts and decomposes at 98—99°. A. McK.

Quinonedimethylimine. (Quinonoid Compounds. IV.) RICHARD WILLSTÄTTER and ADOLF PFANNENSTIEL (*Ber.*, 1905, **38**, 2244—2251. Compare Abstr., 1904, i, 511, 1050; this vol., i, 361).—In the preparation of *s*-ditoluene-*p*-sulphonyl-*p*-phenylenediamine (Reverdin and Crépieux, Abstr., 1901, i, 686) from toluene-*p*-sulphonic chloride and *p*-phenylenediamine, two by-products are formed in small quantity. One is *toluene*-p-*sulphonyl*-p-*phenylenediamine toluene*-p-*sulphonate*,

$$C_{20}H_{22}O_5N_2S_5,$$

which crystallises in hard, nacreous prisms; the other is *toluene*-p-*sulphonyl*-p-*phenylenediamine*, which crystallises from dilute alcohol in needles, and melts at 183° (compare Morgan and Micklethwait, Trans., 1905, **87**, 1303).

Ditoluene-p-*sulphonyl*-s-*dimethyl*-p-*phenylenediamine*,

$$C_6H_4(NMe\cdot SO_2\cdot C_7H_7)_2,$$

prepared by methylating toluene-*p*-sulphonyl-*p*-phenylenediamine by means of methyl sulphate, crystallises from acetone in prisms, and melts at 216°. On hydrolysis with concentrated sulphuric acid, it gives *dimethyl*-p-*phenylenediamine*, $C_6H_4(NHMe)_2$, which crystallises from light petroleum in colourless leaflets, melts at 53°, and boils at 149—150° under 17 mm. pressure; the *dihydrochloride* forms colourless needles, the *picrate* melts at 186°, and the *dinitrosoamine* forms prisms, and melts at 148°.

Methyl-*p*-phenylenediamine, $NH_2\cdot C_6H_4\cdot NHMe$, prepared by reducing *p*-nitrosomethylaniline with tin and hydrochloric acid, forms snow-white leaflets, melts at 35·5°, and boils at 152° under 20 mm. pressure. Bernthsen and Goske (Abstr., 1887, 666) described it as an uncrystallisable oil.

Quinonedimethyldi-imine, $C_6H_4(NMe)_2$, prepared by oxidising *s*-dimethyl-*p*-phenylenediamine dissolved in ether with silver oxide, or, better, by oxidising the same base in light petroleum with lead peroxide, separates in colourless crystals, and melts at 92·5—93° to a dark red liquid; its solutions are coloured yellow, and it is rapidly decomposed by water or alcohol. On adding concentrated hydrochloric or sulphuric acid, it explodes; it is decomposed by hot dilute sulphuric acid, giving *p*-benzoquinone and formaldehyde.

With hydrogen chloride in ethereal solution, it gives a flocculent, reddish-brown substance which dissolves in water to an intense red solution. It does not possess the volatility of quinonedi-imine.

Quinonemonomethylimine, prepared by oxidising *p*-methylamino phenol (metol) with silver oxide or lead peroxide, crystallises from ether on rapid evaporation in slender needles; it is explosive and could not be analysed. W. A. D.

Phenylhydrazine Derivatives of Aconic Acid. HANS REITTER and FRIEDRICH BENDER (*Annalen*, 1905, **339**, 373—379).—The interaction between phenylhydrazine and aconic acid (Abstr., 1895, i, 128) was incorrectly interpreted; the phenylhydrazide of β-aldehydopropionic phenylhydrazone was formed thus: $CO_2H\cdot C{<}^{CH-O}_{CH_2\cdot CO}$ +

$$2NHPh\cdot NH_2 = CO_2 + H_2O + N_2HPh{:}CH\cdot CH_2\cdot CH_2\cdot CO\cdot N_2H_2Ph.$$

When methyl aconate is boiled in methyl-alcoholic solution with phenylhydrazine, the phenylhydrazidephenylhydrazone,

$$NHPh{\cdot}N{:}CH{\cdot}CH(CO_2Me){\cdot}CH_2{\cdot}CO{\cdot}N_2H_2Ph,$$

of the β-monomethyl ester of γ-hydroxyitaconic acid is formed, and, as previously described, melts at 167°. At the same time, a compound, $C_{17}H_{16}O_4N_2$, is produced, and forms the main product of the reaction if the boiling is prolonged, the use of a larger quantity of methyl alcohol causing the formation only of the former; it crystallises in aggregates of needles or thin prisms melting at 186—190°. It is probably a pyrazolone derivative, thus: $N_2H_2Ph{\cdot}CO{\cdot}CH_2{\cdot}CH<\begin{matrix}CH{:}N\\ CO{-}NPh\end{matrix}$.

K. J. P. O.

Action of Hydroxylamine Hydrochloride on Naphthaphenoxazone. FRIEDRICH KEHRMANN and H. DE GOTTRAU (*Ber.*, 1905, **38**, 2574—2578).—The compound described by O. Fischer and Hepp (Abstr., 1903, i, 654) as naphthaphenoxazone oxime is shown to be aminonaphthaphenoxazone, $O<\begin{matrix}C_6H_3{:}N\\ O{-\!-\!-}C_{10}H_5{\cdot}NH_2\end{matrix}$, isomeric with Kehrmann and Gauhe's 2-aminophenonaphthoxazone (Abstr., 1898, i, 45). The by-product obtained by Fischer and Hepp is naphtharesorufin.

The question of the quinonoid or oxonium constitution of azoxazones and also of oxazine and thiazine dyes is discussed. Hantzsch's views (this vol., i, 605) are not accepted.

J. J. S.

Compound of Antipyrine with Mercuric Oxide. CHARLES ASTRE and JULES VILLE (*Bull. Soc. chim.*, 1905, [iii], **33**, 842—845).—The compound $Hg\left[NMe(OH)<\begin{matrix}CMe{:}CH\\ NPh{\cdot}CO\end{matrix}\right]_2$ is obtained when mercuric oxide is heated on the water-bath with an aqueous solution of antipyrine. It crystallises from absolute alcohol in short prisms melting at 195—196°, is only very sparingly soluble in water, ether, or benzene, and its aqueous solution has a faintly alkaline reaction. It does not give the usual reaction of mercuric salts, although it yields a black precipitate with hydrogen sulphide; it gives the usual antipyrine tests. With hydrogen chloride, it yields two definite compounds, one with 3HCl and a second with 4HCl; the latter melts at 87—88°.

J. J. S.

Cyano-derivatives of Pyrimidine. EMANUEL MERCK (D.R.-P. 158591. Compare following abstracts).—Dicyanodiamide reacts with esters of cyanoacetic, malonic, or acetoacetic acids or their derivatives to form pyrimidine derivatives. Thus dicyanodiamide, ethyl cyanoacetate, and sodium ethoxide react in alcoholic solution:

$$CN{\cdot}NH{\cdot}C<\begin{matrix}NH\\ NH_2\end{matrix} + CN{\cdot}CH_2{\cdot}CO_2Et = CN{\cdot}NH{\cdot}C<\begin{matrix}N{-}C(OH)\\ N{:}C(NH_2)\end{matrix}>CH.$$

2-*Cyanamino*-4-*amino*-6-*hydroxypyrimidine* forms colourless crystals which decompose without melting when heated. The *sodium* salt is crystalline. 2-*Cyanamino*-6-*hydroxy*-4-*methylpyrimidine*, from dicyanodiamide and ethyl acetoacetate, forms colourless crystals and melts and

decomposes at about 265°. 2-*Cyanamino*-4 : 6-*dihydroxypyrimidine*, from ethyl malonate, forms colourless crystals and decomposes when heated.

The cyano-compounds yield carboxylic acids on hydrolysis. The cyanamino-group may be replaced by oxygen, yielding barbituric acid derivatives. C. H. D.

2 : 4-Di-imino-6-hydroxy-5 : 5-dialkylpyrimidines. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 158592).—Dialkylated cyanoacetic esters condense with guanidine in presence of sodium ethoxide to form pyrimidine derivatives.

2 : 4-*Di-imino*-6-*hydroxy*-5-*diethylpyrimidine*,

$$NH<\begin{matrix}C(NH)-NH\\C(NH)\cdot CEt_2\end{matrix}>CO,$$

melts at 295° and dissolves sparingly in organic solvents or dilute alkalis, more readily in boiling water; it forms crystalline salts with strong acids. 2 : 4-*Di-imino*-6-*hydroxy*-5-*dimethylpyrimidine* is insoluble in alcohol or ether, but dissolves readily in dilute alkalis and forms crystalline salts with acids.

The imino-groups are readily eliminated from these compounds on hydrolysis, and dialkylbarbituric acids are thus obtained. C. H. D.

Di-iminothiopyrimidine and its Alkyl Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 158621. Compare preceding abstracts).—Malononitrile and its alkyl derivatives react with thiocarbamide in presence of alkaline condensing agents, yielding di-iminothiopyrimidine and its derivatives.

4 : 6-*Di-imino*-2-*thiopyrimidine*, $CH_2<\begin{matrix}C(NH)\cdot NH\\C(NH)\cdot NH\end{matrix}>CS$, from malononitrile, thiocarbamide, and alcoholic sodium ethoxide, separates from dilute acetic acid in white needles, dissolves sparingly in water or alcohol, and is insoluble in ether, benzene, or chloroform.

4 : 6-*Di-imino*-2-*thio*-5 : 5-*diethylpyrimidine*, prepared in similar manner from diethylmalononitrile, crystallises from water in yellow needles and melts and decomposes at 230°. The *dipropyl* derivative is a yellow, crystalline powder melting at 227°. The *monoethyl* derivative melts and decomposes at 292°. C. H. D.

Piperazine Monomethylarsonate. A. ASTRUC (*Bull. Soc. chim.*, 1905, [iii], 33, 839—842. Compare this vol., i, 382).—*Piperazine methylarsonate*, $[(OH)_2AsMeO]_2,C_4H_{10}N_2,2H_2O$, is formed when a solution of piperazine in cold alcohol is mixed with a hot alcoholic solution of methylarsonic acid. It crystallises in slender, white needles, effloresces at about 95—100°, loses its water of crystallisation, and then melts at 130°. It is soluble in its own weight of distilled water and the solution has an acid reaction towards phenolphthalein but basic towards Poirier-Orange No. 3. It yields precipitates with normal or basic lead acetate, silver nitrate, mercuric chloride, picric acid, or uranium acetate. J. J. S.

New Constituent of Milk. I. G. BISCARO and E. BELLONI (*Chem. Centr.*, 1905, ii, 63—64; from *Mon. Scient.*, [iv], 19, i, 384).—The

occurrence of small crystals of an organic compound in the mother liquor of lactose has led to the discovery of a new acid, orotic acid, which has been found to be a normal constituent of milk. The acid was isolated in the form of its lead salt, from which the free acid was obtained by means of hydrogen sulphide. This compound has probably hitherto escaped detection owing to the solubility of the lead salt in water. The presence of a large proportion of potassium compounds in milk in comparison with blood, urine, &c., is due to the presence of orotic acid, which has a strong affinity for potassium, which it withdraws from the tissues. *Orotic acid*, $C_5H_4O_4N_2,H_2O$, prepared by the action of sulphuric acid on the potassium salt contained in milk, forms crystals, and decomposes at 260°; it is sparingly soluble in water and insoluble or only very slightly soluble in organic solvents. Since by the action of potassium permanganate it yields carbamide, it is probably a monoureide (compare Abstr., 1900, ii, 322). When reduced with hydrogen iodide, it forms a ketone containing the group $-CH_2\cdot CO$. The *potassium* salt, $C_5H_3O_4N_2K$, is crystalline, and sparingly soluble in cold water. The *sodium* salt, $C_5H_3O_4N_2Na$, crystallises in large needles and, when mixed with solutions of potassium salts, forms the corresponding potassium orotate. The *silver* salt, $C_5H_3O_4N_2Ag,H_2O$, prepared by adding silver nitrate to a solution of the potassium salt, forms a white, amorphous precipitate. The *normal silver* salt, $C_5H_2O_4N_2Ag_2,H_2O$(?), obtained by adding silver nitrate to a solution of the normal potassium salt, which is prepared by heating the sodium salt with potassium hydroxide, forms a white precipitate. The *lead* salt, $C_5H_2O_4N_2Pb$, is a white precipitate and is somewhat soluble in water. E. W. W.

Orotic Acid. II. G. BISCARO and E. BELLONI (*Chem. Centr.*, 1905, ii, 64; from *Ann. Soc. Chim. Milano*, 11, 1905. Compare preceding abstract).—Orotic acid is not attacked by the lactic acid ferment nor by the process of lactic fermentation. Two *barium* salts, $(C_5H_2O_4N_2)_2Ba$ and $C_5H_2O_4N_2Ba$, are described. *Methyl orotate*, $C_5H_3O_4N_2Me$, a white, crystalline powder with a somewhat bitter taste, melts at 248—250° and dissolves in water or alcohol, forming faintly acid solutions. *Ethyl orotate* is a white, crystalline powder, melting at 200°. *Dichloro-orotic acid*, $C_5H_4O_3N_2Cl_2,H_2O$, prepared by heating potassium orotate with phosphorus oxychloride at 160—165°, crystallises from boiling water in small, yellow needles, is soluble in ether, and melts in its water of crystallisation at 115°. It decomposes at 65° [?165°] and at a higher temperature regenerates orotic acid with elimination of hydrogen chloride. Since the acid contains the $CO(NH)_2$ group and the group $CH_2\cdot CO$, its constitution is probably

$$CO{<}\begin{matrix}NH\cdot CH_2\cdot CO\\ NH{-}CO{-}CO\end{matrix} \quad \text{or} \quad CO{<}\begin{matrix}NH\cdot CO\cdot CH_2\\ NH\cdot CO\cdot CO\end{matrix}.$$

E. W. W.

Aliphatic Derivatives of 1 : 2 : 4-Triazole. GUIDO PELLIZZARI and ANGELO SOLDI (*Gazzetta*, 1905, 35, i, 373—388).—1-*Methyl-1 : 2 : 4-triazole*, $NMe{<}\begin{matrix}CH{:}N\\ N{=}CH\end{matrix}$, prepared by the action of methyl

iodide on a methyl-alcoholic solution of sodium triazole, is a colourless liquid boiling at 178° and having the sp. gr. 1·097 at 24°; on cooling with ice, it solidifies in large, transparent crystals melting at 20°. It is readily soluble in water, alcohol, or ether, and gives with copper sulphate in aqueous solution a blue coloration, with mercuric chloride or silver nitrate a white, crystalline precipitate, with ferric chloride a red coloration, and with oxalic and nitric acids readily soluble salts. Its *hydrochloride*, $C_3H_5N_3,HCl$, separates from a mixture of alcohol and ether as a white, deliquescent substance with no sharp melting point. The *platinichloride*, $(C_3H_5N_3)_2,H_2PtCl_6,5H_2O$, forms orange-yellow, acicular crystals, and in the anhydrous condition melts at 165° and decomposes at a slightly higher temperature. *Tetrachloroplatinimethyltriazole*, $(C_3H_5N_3)_2PtCl_4$, obtained by the action of either hot water or heat on the platinichloride, separates in small, pale yellow, insoluble crystals. The constitution of 1-methyl-1 : 2 : 4-triazole has been settled by preparing it by the interaction of diformylmethylhydrazide and formamide.

1-*Ethyl*-1 : 2 : 4-*triazole*, $C_4H_7N_3$, prepared by the action of ethyl bromide on an alcoholic solution of sodium triazole, is a colourless liquid boiling at 182·5°, having the sp. gr. 1·046 at 18° and dissolving readily in water, alcohol, or ether. Its *platinichloride*, $(C_4H_7N_3)_2H_2PtCl_6,2H_2O$, separates in yellow, slender needles or shorter crystals melting and decomposing at 160—165°. *Tetrachloroplatiniethyltriazole*, $(C_4H_7N_3)_2PtCl_4$, forms microscopic, yellow crystals.

1-*Allyl*-1 : 2 : 4-*triazole*, $C_5H_7N_3$, is a colourless liquid boiling at 198°, having the sp. gr. 1·056 at 18° and dissolving readily in water, alcohol, or benzene. Its *platinichloride*, $(C_5H_7N_3)_2,H_2PtCl_6,H_2O$, separates from hydrochloric acid in well-formed prisms melting and decomposing at 112—115°. *Tetrachloroplatiniallyltriazole*, $(C_5H_7N_3)_2PtCl_4$, separates in canary-yellow, silky needles; if boiled for some hours with water, this compound loses a further quantity of 3HCl, giving a compound of the composition $(C_5H_5N_3)_2PtCl_2$. T. H. P.

Action of Semicarbazide on Benzil, Benzoin, and Allied Substances. HEINRICH BILTZ (*Annalen*, 1905, **339**, 243—294).—With a dilute alcoholic solution of semicarbazide, benzil yields at the ordinary temperature a monosemicarbazone, but at a higher temperature a mixture of disemicarbazone and 5 : 6-diphenyl-3-oxy-1 : 2 : 4-triazine. Although the acetate of the latter is probably an *O*-ester, $CPh{<}^{CPh:N}_{N\text{—}N}{>}C\cdot OAc$, the methyl and ethyl ethers are found to be *N*-ethers, $CPh{<}^{CPh:N}_{N-NR}{>}CO$.

The action of semicarbazide on benzoin is more complicated; at the ordinary temperature, the simple semicarbazone is formed; at higher temperatures, an additive product of oxydiphenyltriazine with 4 : 5-diphenyliminazolone, $\begin{matrix}CPh\cdot NH\\ \|\\ CPh\cdot NH\end{matrix}{>}CO$, and oxydiphenyltriazine are formed according to the conditions. Anisil yields a semicarbazone and an oxytriazine, whilst anisoin gives a semicarbazone. Corresponding compounds are formed from piperil, cuminil, and cuminoin.

On reduction with zinc and acetic acid, the oxytriazines yield dihydro-oxytriazines, $CPh\!\!<\!\!\begin{matrix}CHPh\cdot NH\\N\text{——}NH\end{matrix}\!\!>\!\!CO$; further reduction could not be effected, but on treatment with hydriodic acid and phosphorus, ammonia and diphenyliminazolone are produced.

[With Thankmar Arnd.]—*Benzilmonosemicarbazone*, $C_{15}H_{13}O_2N_3$, prepared by keeping an aqueous solution of benzil, semicarbazide hydrochloride, and potassium acetate for three days, crystallises in colourless plates melting at 174—175° and is decomposed by hydrochloric acid. When heated in alcoholic solution, the semicarbazone is converted into 3-oxy-5 : 6-diphenyltriazine, which crystallises in pale yellow crystals melting at 225—226°; the *sodium* derivative crystallises in pale yellow needles; the *hydrobromide* forms six-sided plates and the *nitrate* deep yellow crystals; the *hydrochloride* is unstable. The O-*acetyl* derivative crystallises in colourless prisms melting at 154° and readily hydrolysed by sodium hydroxide. 3-*Oxy*-5 : 6-*diphenyl*-2-*methyltriazine* is prepared from the triazine, methyl sulphate, and sodium methoxide in methyl alcohol, and forms colourless crystals melting and decomposing at 152—153°; it dissolves unchanged in concentrated acids. The *disemicarbazone* of benzil, $C_{16}H_{16}O_2N_6$, prepared by boiling benzil in diluted alcohol with semicarbazide hydrochloride and potassium acetate and removing the oxydiphenyltriazine by means of sodium hydroxide, forms leaflets melting and decomposing at 243—244°.

Benzoinsemicarbazone, $C_{15}H_{15}O_2N_3$, crystallises in prisms melting and decomposing at 206°, and on hydrolysis with hydrochloric acid yields hydrobenzoin. The *additive* product, $C_{30}H_{23}O_2N_5$, of oxydiphenyltriazine and 4 : 5-diphenyliminazolone is produced when benzoin in alcoholic solution is boiled with semicarbazide hydrochloride and potassium acetate for several hours, and the product crystallised from chloroform, the oxydiphenyltriazine being left in the mother liquor; it crystallises in pale yellow needles melting at 258—259°. If the potassium acetate is absent, then a substance, probably tolanediurein, which melts at 350°, together with the iminazolone and a compound melting at 247—248°, and occasionally oxydiphenyltriazine, are produced. The additive product above mentioned is decomposed into its components by heating with acetic acid, and can be again regenerated from them. 4 : 5-Diphenyliminazolone melts at 323—324°, fluoresces in dilute solution, and reduces ammoniacal silver solution. The *diacetyl* derivative, $C_{19}H_{16}O_3N_2$, crystallises in needles, and the *dibenzoyl* derivative, which is formed in pyridine solution, forms colourless crystals melting at 250—251°.

[With Carl Stellbaum.]—4 : 5-Diphenyliminazolone is readily prepared by heating benzoin with carbamide in acetic acid solution; the 4 : 5-*dimethoxy*-derivative, $C_{17}H_{16}O_3N_2$, prepared from anisoin and carbamide, crystallises in colourless needles melting at 284°. 4 : 5-*Dimethylenetetroxydiphenyliminazolone*, $C_{17}H_{12}O_5N_2$, prepared from piperoin, crystallises in needles melting at 291°. Cuminoin yields 4 : 5-*di*-iso*propyldiphenyliminazolone*, $C_{21}H_{24}ON_2$, crystallising in needles melting at 294—295°.

[With Thankmar Arnd.]—At the ordinary temperature or on warm-

ing at 80°, semicarbazide and anisil do not react, but at 100° the disemicarbazone, $C_{18}H_{20}O_4N_6$, is produced, crystallising in leaflets melting and decomposing at 254—255°. At the same time, 3-*hydroxy-5 : 6-dimethoxydiphenyltriazine*, $\begin{matrix} OMe\cdot C_6H_4\cdot C\colon N\cdot C\cdot OH \\ OMe\cdot C_6H_4\cdot C\colon N\cdot N \end{matrix}$, is formed as lemon-yellow prisms melting and decomposing at 261—262°. The *sodium* salt crystallises in yellow needles and the *acetyl* derivative in lemon-yellow leaflets melting and decomposing at 157°. The *semicarbazone* of anisoin is formed at the ordinary temperature, and crystallises in prisms melting at 185°.

Piperilmonosemicarbazone could not be prepared, but the *disemicarbazone*, $C_{18}H_{16}O_6N_6$, formed at 100°, crystallises in leaflets melting at 250°; at the same time, 3-*hydroxy*-5 : 6-*dimethylenetetroxydiphenyltriazine*, $\begin{matrix} CH_2\colon O_2\colon C_6H_3\cdot C\colon N\cdot C\cdot OH \\ CH_2\colon O_2\colon C_6H_3\cdot C\colon N\cdot N \end{matrix}$, is obtained, crystallising in lemon-yellow prisms melting at 248°. The *sodium* salt crystallises in yellow needles, and the *acetyl* derivative, $C_{19}H_{13}O_6N_3$, in orange-yellow leaflets melting and decomposing at 208°.

[With Carl Stellbaum.]—Semicarbazide and cuminil only react at 100°, the *disemicarbazone*, $C_{22}H_{28}O_2N_6$, being obtained as leaflets melting and decomposing at 251—252°. 3-*Hydroxy*-5 : 6-*di*iso*propyldiphenyltriazine*, $\begin{matrix} C_6H_4Pr^{\beta}\cdot C\colon N\cdot C\cdot OH \\ C_6H_4Pr^{\beta}\cdot C\colon N\cdot N \end{matrix}$, crystallises in yellow rhombohedra melting at 250—251°. The *acetyl* derivative crystallises in yellow needles melting at 136—137°. *Cuminoinsemicarbazone*, $C_{21}H_{27}O_2N_3$, crystallises in needles melting and decomposing at 210°.

On reducing oxydiphenyltriazine with zinc foil and acetic acid, 3-*oxy*-5 : 6-*diphenyldihydrotriazine* is obtained, crystallising in needles melting at 275—276°; it is also produced by boiling benzoin and semicarbazide in dilute acetic acid solution. The *diacetyl* derivative forms colourless needles melting at 138°, and the *dibenzoyl* derivative colourless prisms melting at 188—189°. The *methyl* ether can only be obtained indirectly by reducing oxydiphenyltriazine methyl ether and forms crystals melting at 199°. 3-*Oxy*-5 : 6-*dimethoxydiphenyldihydrotriazine*, $C_{17}H_{17}O_3N_3$, prepared by reduction of the corresponding triazine, crystallises in needles melting at 212—213°; the *diacetyl* derivative crystallises in needles melting at 132°, and the *dibenzoyl* derivative forms crystals melting at 194—195°. 3-*Oxy*-5 : 6-*dimethylenetetroxydiphenyldihydrotriazine*, $C_{17}H_{13}O_5N_3$, prepared by reduction of oxydimethylenetetroxydiphenyltriazine, forms crystals melting at 285°. The *diacetyl* derivative forms crystals melting at 163° and the *dibenzoyl* derivative crystals melting at 212—213°. 3-*Oxy*-5 : 6-*di*iso*propyldiphenyldihydrotriazine*, $C_{21}H_{25}ON_3$, prepared by reduction of the corresponding triazine or by boiling cuminoin and semicarbazide, crystallises in colourless needles melting at 255—256°; the *diacetyl* derivative crystallises in needles melting at 123°, and the *dibenzoyl* derivative forms crystals from acetone melting at 188°.

On reducing oxydiphenyldihydrotriazine with hydriodic acid and red phosphorus, 4 : 5-diphenyliminazolone is produced and forms crystals melting at 323—324°. K. J. P. O.

A Condensation Product of Phenylmethylpyrazolone. ERNST MOHR (*Ber.*, 1905, 38, 2578—2579).—Small quantities (10 grams) of 1-phenyl-3-methylpyrazolone distil at 191° under 17 mm. pressure without decomposing. But with larger quantities (100—150 grams) decomposition occurs, and crystals are deposited in the upper part of the flask. The amount of crystalline compound is increased by heating the pyrazolone at 250° for four hours in a reflux apparatus through which a current of dry air is passed, distilling off the more volatile products under reduced pressure, extracting the residue with about five times its weight of absolute alcohol, and then repeatedly crystallising from boiling alcohol or xylene. It has the composition $C_{20}H_{18}ON_4$ = $\begin{array}{l}CMe\cdot CH_2\\ \| \\ N\text{——}NPh\end{array}\!\!>C{:}C<\!\!\begin{array}{l}CMe{:}N\\ \quad\ \ | \\ CO\text{—}NPh\end{array}$, and crystallises in practically colourless prisms, melts at 260°, is only sparingly soluble in hot chloroform, benzene, or xylene, somewhat more readily in boiling alcohol, and readily in hot aniline or acetic acid, and possesses both basic and acidic properties. J. J. S

Transformation of Azoxybenzaldehyde. FRIEDRICH J. ALWAY and WALTER D. BONNER (*Ber.*, 1905, 38, 2518—2520).—Human and Weil (Abstr., 1904, i, 115) suppose that molecular rearrangement of *m*- and *p*-azoxybenzaldehydes by means of concentrated sulphuric acid takes place according to the equation

$$CHO\cdot C_6H_4\cdot N_2O\cdot C_6H_4\cdot CHO = CHO\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot CO_2H.$$

According to the authors, this is incorrect; the products of the transformations in question are dyes, and possess the properties characteristic of hydroxyazo-compounds. The authors further have prepared *m*-benzaldehydeazobenzoic acid and *p*-benzaldehydeazobenzoic acid, and proved that those compounds are not dyes and that they have properties different from those of the products obtained from the transformation of *m*- and *p*-azoxybenzaldehydes.

m-*Benzaldehydeazobenzoic acid*, $CHO\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot CO_2H$, prepared by the condensation of *m*-nitrosobenzaldehyde with *m*-aminobenzoic acid or by the hydrolysis of its ethyl ester, forms yellow needles and melts at 230° (corr.). Its *ethyl ester*, prepared from *m*-nitrosobenzaldehyde and ethyl *m*-aminobenzoate, forms reddish-yellow needles, and melts at 90° (corr.), whilst its *phenylhydrazone* melts at 195° (corr.).

The transformation product of *m*-azoxybenzaldehyde melts at 165° (corr.), is soluble with difficulty in a cold aqueous solution of sodium carbonate, and is a true dye. The *bisphenylhydrazone* melts at 234° (corr.), the *dioxime* at 207—211° (corr.), the *dianilide* at 141° (corr.), and the *monoanilide* at 126—130° with decomposition. The substance probably has the formula $CHO\cdot C_6H_4\cdot N{:}N\cdot C_6H_3(OH)\cdot CHO$.

p-*Benzaldehydeazobenzoic acid*, prepared by the condensation of *p*-nitrosobenzaldehyde with *p*-aminobenzoic acid or of *p*-aminobenzaldehyde with *p*-nitrosobenzoic acid, is a reddish-yellow powder and does not melt below 300°. The *ethyl ester* forms red crystals, and melts at 159° (corr.). A. McK.

Organic Chemistry.

Catalytic Decomposition of Alkyl Haloïds by means of Anhydrous Metallic Chlorides. Paul Sabatier and Alphonse Mailhe (*Compt. rend.*, 1905, **141**, 238—241. Compare Abstr., 1904, i, 277, 303).—When the vapour of *iso*butyl chloride is passed over dry barium chloride heated at 300°, hydrogen chloride and *iso*butylene are produced. A small proportion of the *iso*butylene undergoes condensation to various hydrocarbons of petroleum-like odour, and it shows a tendency to recombine with the hydrogen chloride in the exit tube, forming either *iso*butyl chloride or one of its isomerides. Similar catalytic reactions take place with the vapours of ethyl, propyl, or *iso*amyl chlorides, but not with methyl chloride. These reactions also occur when barium chloride is replaced by a chloride of one of the bivalent metals, nickel, cobalt, iron, cadmium, or lead, but not with a chloride of the univalent metals, silver, potassium, or sodium. The alkyl bromides are similarly decomposed by anhydrous chlorides or bromides of the bivalent metals at 320°, and the alkyl iodides in presence of anhydrous chlorides, bromides, or iodides of the bivalent metals at temperatures above 300°.

It is suggested that in these reactions a temporary organo-metallic compound of the type $BaCl{\cdot}C_nH_{2n}Cl$ is formed; the latter then dissociates into the metallic chloride and the olefinic hydrocarbon.

As evidence for the view that these temporary organo-metallic derivatives are formed, it is pointed out that anhydrous aluminium chloride dissolves in *iso*butyl chloride at 0°, forming a dark liquid, which evolves butylene and hydrogen chloride, and that anhydrous ferric chloride reacts vigorously with the vapour of *iso*butyl chloride at 300°, evolving hydrogen chloride and forming a dark solid, which is regarded as being produced by the condensation of the organo-metallic compound first formed. Chromic chloride exerts no catalytic action on alkyl chlorides at 300°. T. A. H.

Basic Properties of Oxygen: Compounds of Organic Substances containing Oxygen with Nitric, Sulphuric, and Chlorosulphonic Acids. Douglas McIntosh (*J. Amer. Chem. Soc.*, 1905, **27**, 1013—1016. Compare Trans., 1905, **87**, 784).—The following compounds of nitric acid with ether, alcohol, and acetone have been prepared by adding the acid at −50° to the organic liquid cooled to −80°.

With ethyl ether, a white *compound*, probably $C_4H_{10}O,2HNO_3$, is obtained which melts at −25°, and at higher temperatures undergoes oxidation. It is shown that the liquid compound prepared by Cohen and Gatecliff (Proc., 1904, **20**, 194) at a comparatively high temperature must have contained water.

Ethyl alcohol yields a white, crystalline *compound* which melts at −30°, and probably has the constitution $C_2H_6O\colon HNO_3$. Acetone furnishes a similar *compound*, $C_3H_6O\colon HNO_3$, melting at −18°.

When anhydrous sulphuric acid is added to the cooled organic substances, syrupy liquids are produced.

By the action of chlorosulphonic acid on alcohol at a low temperature, ethyl hydrogen sulphate and hydrogen chloride are formed. Ether and acetone, however, yield white, crystalline *compounds*, $2C_4H_{10}O,HClSO_3$ and $2C_3H_6O,HClSO_3$, which melt at $-45°$ and $-30°$ respectively. E. G.

Esterification by means of Methyl Sulphate. CARL GRAEBE (*Annalen*, 1905, **340**, 244—249).—After an historical *résumé* of the observations which have been made on the preparation of methyl esters by means of methyl sulphate, an account is given of a series of experiments on the methylation of benzoic acid by this reagent.

Solutions of the salts of benzoic acid, when shaken or when heated with methyl sulphate, give but small yields of the methyl ester. If the solid salts are heated with methyl sulphate at first at 160° and finally at 205—210°, until distillation ceases, quantitative yields are obtained. Both the methyl groups of the methyl sulphate are used in forming the ester. Potassium benzoate gives better results than the sodium salt. Acetic acid gives exactly similar results. Tetrachlorophthalic acid is converted into its methyl ester when either a solution of its salts or the dry salt is treated with methyl sulphate. The same applies to naphthalic acid, which gives but poor yields of the ester. Chloroanilic acid can only be esterified by heating the dry potassium salt at 100° with methyl sulphate. K. J. P. O.

Reduction of Oleic Acid to Stearic Acid by Electrolysis. JULIUS PETERSEN (*Chem. Centr.*, 1905, ii, 304—305; from *Overs. K. Danske Videnskabernes Selsk. Forh.*, 1905, 137—149).—By the electrolytic reduction of oleic acid, stearic acid is formed. A good yield of the latter is obtained when a mixture of a solution of 10 grams of oleic acid in 150 c.c. of alcohol with 3 c.c. of dilute sulphuric acid is electrolysed at 32°, using a current of 1·35 amperes at about 20 volts. The cell is provided with a diaphragm and the platinum anode immersed in sulphuric acid; the cathode is of nickel gauze. The oleic acid is most readily reduced when the quantity of sulphuric acid is small. A better yield is obtained, however, when hydrochloric acid is used, and in this case 5 c.c. of a normal solution are added to 100 c.c. of the alcoholic solution of oleic acid and the mixture electrolysed with a current of 0·13 amperes. If the electrolysis is prolonged, the quantity of acid reduced decreases after a time. The longer the solution has been allowed to remain with hydrochloric acid before electrolysing the more readily is it reduced by the current, possibly owing to the formation of chlorostearic acid. In an experiment in which hydrochloric acid was added slowly, drop by drop, in order to maintain the *E.M.F.* at about 20 volts, the current being one ampere and the temperature 30—35°, stearic acid separated out in seven hours. Increase of current density decreases the yield, but it is not affected by variation of temperature. Solutions of alkali oleates are not conveniently electrolysed owing to the formation of froth.

E. W. W.

Ammonium Oxalate; its Formula and Stability. P. V. Dupré (*Analyst*, 1905, **30**, 266—273).—The salt is found to have the formula $(NH_4)_2C_2O_4,H_2O$ under all conditions of crystallisation. When heated in ordinary air it remains stable up to a temperature of from 30° to 40°, but above this temperature water is lost very slowly. In perfectly dry air, ammonium oxalate loses water even at 12°, although but slowly, whilst at 40° the loss is complete in two days. Under a pressure of one mm. the salt loses all its water in three days at as low a temperature as 6·7°. The rate of dehydration is very nearly constant for any given temperature and approximately doubles for every rise of 10°. The vapour pressure of ammonium oxalate does not reach that of water even at a temperature of 95°, nor that of air saturated to the extent of 75 per cent. with aqueous vapour. The salt is therefore stable at all temperatures up to 95°, provided the air is not less than half saturated with moisture. W. P. S.

Acid Oxalates of Ammonium. Percy T. Walden (*Amer. Chem. J.*, 1905, **34**, 147—152).—An investigation of the acid oxalates of ammonium has been carried out by means of the solubility method described by Foote (Abstr., 1903, i, 797). The results show that the only acid salts which can be prepared from mixtures of ammonium oxalate and oxalic acid in aqueous solution at 25° are

$(NH_4)_2C_2O_4,3H_2C_2O_4,4H_2O$ and $(NH_4)_2C_2O_4,H_2C_2O_4,H_2O$,

both of which have been described by Nichols (*Chem. News*, 1870, **22**, 14). The compound $(NH_4)_2C_2O_4,H_2C_2O_4,2H_2O$, described by Rammelsberg (*Ann. Phys. Chem.*, 1854, **93**, 24), could not be obtained. E. G.

Acid Oxalates of Lithium, Sodium, Potassium, and Cæsium and their Solubility. Harry W. Foote and I. A. Andrew (*Amer. Chem. J.*, 1905, **34**, 153—164).—The stable acid oxalates of lithium, sodium, potassium, and cæsium capable of formation in aqueous solution at 25° have been studied by means of the solubility method described previously (Abstr., 1903, i, 797). The results are tabulated and plotted as curves.

The only salt obtainable from lithium oxalate and oxalic acid is $LiHC_2O_4,H_2O$, which was first described by Rammelsberg (*Annalen*, 1845, **56**, 221). Sodium oxalate and oxalic acid also yield but one salt, $NaHC_2O_4,H_2O$ (Graham, *Annalen*, 1839, **29**, 1). In addition to the two well-known acid potassium oxalates, $KH_3(C_2O_4)_2,2H_2O$ and KHC_2O_4, a third *salt*, $2K_2C_2O_4,H_2C_2O_4,2H_2O$, has been isolated, but is formed only under a narrow range of conditions and cannot be recrystallised. *Cæsium oxalate*, $Cs_2C_2O_4,H_2O$, is soluble in water to the extent of 75·82 per cent. of the anhydrous salt. The following acid salts have been obtained: $CsH_3(C_2O_4)_2,2H_2O$; $Cs_2H_4(C_2O_4)_3$; $CsHC_2O_4$; and $Cs_8H_6(C_2O_4)_7$. E. G.

Certain Alleged Double Oxalates. Harry W. Foote and I. A. Andrew (*Amer. Chem. J.*, 1905, **34**, 164—167).—The double oxalates $KNaC_2O_4$, $K(NH_4)C_2O_4$, and $(NH_4)LiC_2O_4$ have been mentioned in chemical literature, but some doubt has been expressed as to their

existence. It has now been ascertained by means of the solubility method (Abstr., 1903, i, 797) that none of these salts exists at 25°.

A large number of double oxalates of ammonium with magnesium, zinc, and cadmium have been described. An investigation of these salts has been carried out by the solubility method, and it has been found that no double oxalate is formed at 25°, and, further, that owing to the very slight solubility of magnesium, zinc, and cadmium oxalates in saturated solutions of ammonium oxalate it is very improbable that double salts of these oxalates exist at any temperature. E. G.

Synthesis of Dibasic Acids. I. GUSTAVE BLANC (*Bull. Soc. chim.*, 1905, [iii], **33**, 879—897. Compare this vol., i, 15, 115; Bouveault and Blanc, Abstr., 1904, i, 642; this vol., i, 11).—Ethyl αα-dimethylsuccinate and αα-dimethylsuccinic anhydride are reduced by sodium and alcohol, the anhydride the more easily, with formation of (*a*) the corresponding glycol, (*b*) a *substance* which distils together with the alcohol, and could not be obtained in a state of purity; it has a burning taste, an odour resembling that of acetone, is miscible with water, and may be 3 : 3-dimethyltetrahydrofuran; and (*c*) αα-dimethylbutyrolactone mixed with a small proportion of ββ-dimethylbutyrolactone. The lactones, which cannot be separated, form a colourless liquid which boils at 200—201° under the atmospheric pressure, has a penetrating odour, is soluble in much water, and is partly precipitated from its aqueous solution on addition of potassium carbonate. The *barium* salt of the corresponding hydroxy-acid crystallises with $15H_2O$ and is very soluble in water. The *hydrazino-derivative*, $\begin{matrix} CH_2\cdot CMe_2 \\ | \\ CH_2 \text{——} O \end{matrix}\!\!>C(OH)\cdot NH\cdot NH_2$ (compare Blaise and Luttringer, this vol., i, 329), forms small, deliquescent crystals and melts at about 50°. When the lactone mixture is heated with potassium cyanide in a sealed tube at 270° for five hours and the product hydrolysed, there is obtained αα-dimethylglutaric acid, which melts at 85° (compare Perkin and Smith, Trans., 1902, **81**, 256) and forms a *β-naphthylamide* melting at 149—150°, and a small quantity of ββ-dimethylglutaric acid which melts at 102° and forms a *β-naphthylamide* melting at 188—190° and less soluble in alcohol than its isomeride.

The reduction of ethyl αα-dimethylglutarate with sodium and alcohol leads to the formation of the corresponding glycol and of *αα-dimethylvalerolactone*, $\begin{matrix} CMe_2\cdot CO\cdot O \\ | \qquad\quad | \\ CH_2\cdot CH_2\cdot CH_2 \end{matrix}$. This is an oily liquid, which boils at 220° under the atmospheric pressure, has a penetrating odour, and is soluble in water, from its solution in which it is partly precipitated on addition of potassium carbonate. The *barium* salt of the corresponding hydroxy-acid crystallises with $1\frac{1}{2}H_2O$. The action of potassium cyanide on the lactone at 280° and hydrolysis of the resulting nitrile lead to the formation of αα-dimethyladipic acid melting at 87°. No trace of the ββ-isomeride could be found.

α-Methylsuccinic anhydride is reduced by sodium and alcohol to α-methylbutyrolactone (Fichter and Herbrand, Abstr., 1896, i, 463),

which is an oily liquid, boiling at 200—202°. The *hydrazino*-derivative, $\begin{matrix} CH_2\cdot CHMe \\ CH_2 \text{———} O \end{matrix}\!\!>\!C(OH)\cdot NH\cdot NH_2$, crystallises in small scales and melts at 91°. *a*-Methylglutaric acid only was obtained on heating the lactone with potassium cyanide and hydrolysing the product.

Ethyl γ-bromo-αα-dimethylbutyrate, $CH_2Br\cdot CH_2\cdot CMe_2\cdot CO_2Et$, is formed when αα-dimethylbutyrolactone is heated gently with phosphorus pentabromide and the product treated with alcohol. It is a colourless, mobile liquid, possessing a characteristic persistent odour, and boils at 115—116° under 23 mm. pressure When boiled with ethyl sodiocyanoacetate, it forms an unsaturated ester, probably ethyl dimethylvinylacetate, and *ethyl δ-cyano-αα-dimethyladipic acid*,

$$CO_2Et\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CH(CN)\cdot CO_2Et,$$

which, when hydrolysed with alcoholic potassium hydroxide and evaporated to dryness with hydrochloric acid, yields the tricarboxylic acid which is obtained on oxidising dihydro*iso*lauronic acid with sodium hypobromite. When heated at 180°, it loses carbon dioxide, forming αα-dimethyladipic acid.

On boiling αα-dimethyladipic acid with acetyl chloride in a reflux apparatus, the *anhydride* is obtained as a syrup (compare Tiemann, Abstr., 1901, i, 157), which, when heated at 200°, loses carbon dioxide and forms a *substance* which may be dimethyl*cyclo*pentanone. The *anilic acid*, $CO_2H\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO\cdot NHPh$, formed by heating the anhydride with aniline in benzene solution, crystallises in scales and melts at 168°.

The action of ethyl γ-bromo-αα-dimethylbutyrate on ethyl sodiocyanosuccinate leads to the formation of ethyl dimethylvinylacetate and the *cyano*-ester, $CO_2Et\cdot CMe_2\cdot CH_2\cdot CH_2\cdot C(CN)(CO_2Et)\cdot CH_2\cdot CO_2Et$, which boils at 235—240° under 20 mm. pressure, and is hydrolysed easily by boiling hydrochloric acid, with formation of the *acid*, $CO_2H\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$. This crystallises in prisms, and is only slightly soluble in ether or water, but more so in alcohol. With the object of forming dihydro*iso*lauronic acid, this tribasic acid was boiled with acetic anhydride for six hours, the acetic acid and excess of anhydride distilled off in a vacuum, and the residue heated at 240—250°, when there was obtained a viscid liquid distillate which, with semicarbazide in acetic acid solution, formed a *semicarbazone* melting at 215°. The *acid* obtained from the semicarbazone melts at 85°, is isomeric with dihydro*iso*lauronic acid, and may have the constitution $\begin{matrix} CMe_2\cdot CO \\ CH_2\cdot CH_2 \end{matrix}\!\!>\!CH\cdot CH_2\cdot CO_2H$. G Y.

Synthesis of Dibasic Acids. II. GUSTAVE BLANC (*Bull. Soc. chim.*, 1905, [iii], 33, 897—911. See preceding abstract).—αα-Dimethylvalerolactone is obtained in a yield of 25—30 per cent. of the theoretical by reducing αα-dimethylglutaric anhydride. *ββ*-Dimethylvalerolactone, $\begin{matrix} CMe_2\cdot CH_2\cdot CO \\ CH_2\cdot CH_2-O \end{matrix}$, obtained similarly by reduction of ββ-dimethylglutaric anhydride, forms a crystalline mass

resembling camphor, melts at 30°, and boils at 234—235°. When treated successively with potassium cyanide and hydrochloric acid, it yields ββ-dimethyladipic acid and a neutral *substance*, which contains 16·8 per cent. of nitrogen, crystallises in delicate spangles, and decomposes at 250°. The acid is identical with that obtained on oxidation of α-ionone, of geronic acid, and of *iso*geranic acid (Tiemann, Abstr., 1898, i, 374; Tiemann and Schmidt, *loc. cit.*, 377). When heated with a mixture of acetic anhydride and acetyl chloride, it forms the *anhydride*, $C_8H_{12}O_3$, as a viscid, colourless syrup, which with aniline in benzene solution forms an uncrystallisable *anilide*. Noyes' supposed ββ-dimethyladipic acid (Abstr., 1901, i, 631) is probably β-*iso*propylglutaric acid (compare Thorpe, Trans., 1900, **77**, 942). Blaise's ββ-dimethylbutyrolactone (Abstr., 1898, i, 516), boiling at 208°, contains a small proportion of the αα-isomeride; when treated successively with phosphorus pentabromide and absolute alcohol, it forms a mixture of the γ-bromo-esters which boils at 102—104° under 9 mm. pressure and reacts with ethyl sodiocyanoacetate in absolute alcoholic solution to form ethyl 2 : 2-dimethyl*cyclo*propane-1-carboxylate,

$$\begin{array}{l}CMe_2\\ \vert\\ CH_2\end{array}\!\!>CH\cdot CO_2Et,$$

boiling at 70—80° under 9 mm. pressure, and a small quantity of the *cyano-ester*, $CO_2Et\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CH(CN)\cdot CO_2Et$. This boils at 175° under 8 mm. pressure, and on hydrolysis yields the *tricarboxylic acid*, which melts with evolution of carbon dioxide and formation of αα-dimethyladipic acid at 167°.

The product obtained on reducing α-*iso*propylsuccinic anhydride is a mixture of α- and β-*iso*propylbutyrolactones, the latter in the greater proportion. The mixture is a colourless oil which boils at 228—230°, is soluble in six times its weight of water, and forms the mixed *hydrazino*-derivatives, crystallising in small scales and melting at 95°. The corresponding *barium* salts are extremely soluble in water. The α- and β-*iso*propylglutaric acids formed on heating the mixed lactones with potassium cyanide and hydrolysing the nitriles so formed are separated by conversion into their anilides, of which the α-*iso*propylglutaranilide is much more soluble in benzene than its isomeride. These synthetical *iso*propylglutaric acids are racemic, whereas Martine's α-*iso*propylglutaric acid, as well as dihydrocamphoric acid from which it is obtained by oxidation, is optically active (compare Perkin and Crossley, Trans., 1898, **73**, 23). The successive action of phosphorus pentabromide and absolute alcohol on the mixture of lactones obtained by reduction of α-*iso*propylsuccinic anhydride leads to the formation of a mixture of ethyl γ-bromo-α-*iso*propylbutyrate and its β-*iso*propylisomeride, which is a colourless oil boiling at 110° under 10 mm. pressure. On heating the mixture of bromo-esters with ethyl sodiocyanoacetate and distilling the product, two fractions are obtained: the first contains an *unsaturated* ester together with unchanged bromo-ester and boils at 90—95° under 10 mm. pressure; the second boils at 188—190° under 10 mm. pressure, and on hydrolysis with alcoholic potassium hydroxide and treatment with hydrochloric acid yields a considerable quantity of regenerated lactone and only very little of the *tricarboxylic acid*, $C_{10}H_{16}O_6$, melting and decomposing at

145°. It must be, therefore, a mixture of ethyl cyano*iso*propyladipate and a product of the structure

$$CN\cdot CH\dot{:}C(OEt)\cdot O\cdot CH_2\cdot CH_2\cdot CHPr^{\beta}\cdot CO_2Et.$$

Better results are obtained by condensing the γ-bromo-esters with ethyl sodiomalonate, when there are obtained the fraction mentioned previously, boiling at 90—95° under 10 mm. pressure, and the *tricarboxylic* ester, $C_{16}H_{28}O_6$, which boils at 185° under 8 mm. pressure and on hydrolysis yields the tricarboxylic acid crystallising in prisms and melting and decomposing at 145°. *a-iso*Propyladipic acid, $C_9H_{16}O_4$, formed when the tricarboxylic acid is heated at 180°, crystallises in small prisms and melts at 63°. Ethyl γ-bromo-*a-iso*propylbutyrate condenses with ethyl sodiomethylmalonate to form the *tricarboxylic* ester, $CO_2Et\cdot CHPr^{\beta}\cdot CH_2\cdot CH_2\cdot CMe(CO_2Et)_2$, which boils at 188—190° under 15 mm. pressure and on hydrolysis yields the *tricarboxylic acid,* $C_{11}H_{18}O_6$. This crystallises from formic acid in small prisms, melts and decomposes at 158°, and when heated at 180° loses carbon dioxide and is converted into *r-cis*-dihydrocamphoric acid,

$$CO_2H\cdot CHPr^{\beta}\cdot CH_2\cdot CH_2\cdot CHMe\cdot CO_2H,$$

melting at 103°. The aqueous mother-liquors from the crystallisation of this contain a resinous isomeric acid which is probably a mixture of the *cis*- and *trans*-forms of dihydrocamphoric acid.

Campholide, which melts at 210°, and when treated with hydrogen bromide forms δ-bromocampholic acid, is obtained by reduction of camphoric acid or of its *ortho*-methyl ester, but not of the *allo*-methyl ester. G. Y.

Action of Sodium Sulphite on Acetaldehyde. ALPHONSE SEYEWETZ and BARDIN (*Compt. rend.*, 1905, **141**, 259—260).—Acetaldehyde does not react with sodium sulphite when the two reagents are mixed in dilute aqueous solution, but with concentrated solutions a vigorous action takes place, the acetaldehyde being converted into crotonaldehyde (40 per cent., compare Orndorff and Newbury, Abstr., 1892, 1423, and Charon, Abstr., 1896, i, 407), aldehyde resin, and a crotonic acid melting at 170—180°. The precautions to be observed in order to obtain the maximum yield of crotonaldehyde are detailed in the original. T. A. H.

Ethoxyacetaldehyde and its Condensation Product with Formaldehyde. ALFRED KLÜGER (*Monatsh.*, 1905, **26**, 879—890).—*Ethoxyacetaldehyde*, $OEt\cdot CH_2\cdot COH$, is obtained by heating ethoxyacetal with 1 mol. of water (slightly acidified by adding 2 drops of concentrated sulphuric acid to 250 c.c. of water) in acetone solution in a sealed tube at 90—95°, shaking the product with calcium chloride, and distilling. It is a transparent, mobile liquid, which boils at 71—73°, has a characteristic suffocating odour, resembling that of acetaldehyde, and reduces ammoniacal silver nitrate. An aqueous solution of ethoxyacetaldehyde is obtained by boiling ethoxyacetal with 2—3 vols. of the above slightly acidified water, in a reflux apparatus, and removing the sulphuric acid by means of barium carbonate. This solution gives the aldehyde reactions, forms silver ethoxyacetate when

boiled with silver oxide, and when treated with 2 mols. of formaldehyde in presence of potassium carbonate yields the *aldol*,

$$OEt\cdot C(CH_2\cdot OH)_2\cdot COH.$$

This is a viscid oil, which decomposes when warmed in air or in a vacuum, is not oxidised on exposure to air, and on reduction with aluminium amalgam yields a slightly yellow *oil*. The *diacetate*, $OEt\cdot C(CH_2\cdot OAc)_2\cdot COH$, is a yellow, viscid, almost odourless oil, which boils at 172—174° under 34 mm. pressure and reduces ammoniacal silver nitrate. G. Y.

Compounds of Ketones with Ammonia. Diethyl Ketone Ammonia. Carl Thomae (*Arch. Pharm.*, 1905, **243**, 393—394. Compare this vol., i, 509).—When a mixture of diethyl ketone with twice its weight of alcohol is saturated with gaseous ammonia and kept for three to four weeks in the dark, the saturation with ammonia being repeated at intervals, and is then exposed in a thin layer for evaporation, an oil remains which has a composition corresponding with the formula $CEt_2(N\colon CEt_2)_2$. In an experiment that lasted three-quarters of a year the yield was 11 per cent. of the theoretical. From a solution of this in ether, gaseous hydrogen chloride precipitates a white, very hygroscopic salt. C. F. B.

Transformation of Dextrose into Lævulose. Detection of Lævulose. Hermann Ost (*Zeit. angew. Chem.*, 1905, **18**, 1170—1178).—Dextrose is partially converted into lævulose by the prolonged action of moderately strong sulphuric acid at the ordinary temperature. The separation of calcium lævulosate is recommended for the detection of lævulose. A. McK.

Influence of Acid, Steam Pressure, and Time on the Production of Dextrose and Dextrin in the Inversion of Potato Starch by Mineral Acids. E. Parow (*Bied. Centr.*, 1905, **34**, 546—548; from *Zeit. Spiritusind.*, 1905, 121).—Starch and 0·8 per cent. of sulphuric acid under 1 atmosphere pressure yielded, after ten minutes, 16·02 per cent. of dextrose and 83·98 per cent. of dextrin; and with 1 per cent. of acid 28·94 per cent. of dextrose and 71·06 per cent. of dextrin. When the action was prolonged for twenty minutes, the amounts of dextrose were 31·06 and 47·24 per cent. with 0·8 and 1·0 per cent. of acid respectively.

Under greater pressure (1·5 and 2 atmospheres) the time is much reduced. In practice, however, a lower pressure is employed in order that the odoriferous substances present may escape. N. H. J. M.

Decomposition Products formed from Starch by Hydrolysis with Hydrochloric Acid; their Estimation in Starch-dextrose and Syrups, and their Influence on the Technical Value of Syrups. Adelbert Rössing (*Chem. Zeit.*, 1905, **29**, 867—873 Compare Abstr., 1904, ii, 298).—The hydrolysis of starch by means of hydrochloric acid yields, under suitable conditions, a new variety of dextrose (δ-*dextrose*), the presence of which may be detected by its undergoing a greater diminution in reducing power when treated with barium

hydroxide than normal dextrose. This diminution, which is due chiefly to the formation of lactic and other organic acids, can be used as a means of estimating dextrose in the presence of dextrin. In addition to δ-dextrose, the hydrochloric acid produces unfermentable, hygroscopic reducing substances (dextrins). The use of syrups prepared by hydrolysis with hydrochloric acid for hard sugar preparations is not to be recommended, for both the dextrose and the salts which are formed during the manufacture exert a deleterious influence, partly through their hygroscopic properties before or after melting, and partly through the inversion of sucrose consequent on the liberation of free acid. An alteration in the proportions of dextrose or dextrin has no influence on solid preparations from normal dextrose syrup. P. H.

Tragacanth and Acacia. Comparative Viscosity of the Simple and Mixed Mucilages. Edmund White (*Pharm. J.*, 1905, [iv], **21**, 133).—The viscosity of a mixture of mucilage of tragacanth and mucilage of acacia is less than that of a corresponding mixture of mucilage of tragacanth and water. This phenomenon appears to be peculiar to tragacanth and does not occur with other gums, such as ghatti, which form viscous mucilages. E. G.

Chicle Gum. Alexander Tschirch and E. Schereschewski (*Arch. Pharm.*, 1905, **243**, 378—393).—Chicle gum is obtained from *Achras sapota*, one of the *Sapotaceæ*, which grows chiefly in Mexico. The sample examined lost 2·33 per cent. when dried at 110°, and gave 4·85 per cent. ash; water dissolved 17, alcohol 60, acetone 62, ether 76, and chloroform 77 per cent. of the drug.

Nothing is present that volatilises with steam. Water extracts a *gum*, mixed with a little proteid substance, which was removed by means of tannic acid; the gum forms 9 per cent. of the drug; it is insoluble in alcohol, optically inactive, yields 3·76 per cent. ash, and gives the α-naphthol sulphuric acid reaction and the reactions for furfuraldehyde. No oxydase is present.

The drug was then extracted repeatedly with boiling alcohol; from the extracts, the alban crystallised on cooling. From the last extracts, *γ-chiclalban*, $C_{15}H_{28}O$, was obtained in small quantity, equal to 0·5 per cent. of the drug; it is crystalline, and melts at 86—87°. The earlier extracts contained a small quantity, equal to 0·2 per cent. of the drug, of a substance sparingly soluble in alcohol at 50°, and melting at 219—221°; this is *α-chiclalban*, $C_{24}H_{40}O$. The bulk of the alban consists of *β-chiclalban*, which crystallises in a variety of forms, and seems, when purest, to form prismatic crystals or round plates which melt at 158° and have the composition $C_{18}H_{30}O$. No cinnamic or other acid was obtained by boiling either the drug or β-chiclalban with alcoholic potassium hydroxide; from the alban, however, a neutral crystalline *substance*, $C_{24}H_{44}O$, melting at 152—153°, was isolated. By concentrating the alcoholic mother-liquor from the alban and pouring it into very dilute hydrochloric acid, *chiclafluavil*, $C_{10}H_{20}O$ or $C_{10}H_{18}O$, was precipitated as a sticky, amorphous substance, which melts at 65—66° when dry; the yield was 1·5 per cent. of the drug.

The residual drug was dissolved in chloroform and the solution poured into alcohol, when *chiclagutta*, $C_{10}H_{16}$, was precipitated; this was crystallised from ether. From the chloroform-alcoholic mother-liquor, *chiclalbanan* separated gradually in small amount; after recrystallising from a mixture of alcohol and ether, it melts at 55—57°.

It is noteworthy that, as with gutta-percha and balata, the fluavil has the lowest, the albanan the highest, percentage of carbon, the albans being intermediate. C. F. B.

Chemical Equilibrium of the System: Ammonia and Primary *iso*Amylamine Hydrochloride. FÉLIX BIDET (*Compt. rend.*, 1905, **141**, 264—265. Compare Abstr., 1901, i, 634).—Dry ammonia is absorbed by primary *iso*amylamine hydrochloride with liberation of the amine and formation of ammonium chloride. The limiting pressures in the reaction are 105 mm. at −23°, 202 mm. at −9·5°, 262 mm. at 0°, and 452 mm. at 16°. Practically identical limiting pressures were also obtained in the inverse action, namely, the interaction of the liquid *iso*amylamine with solid ammonium chloride. It is probable that in these reactions the free base unites with either the ammonium chloride or the amine hydrochloride. No molecular compound of this type was isolated, but it was observed that heat is developed when primary *iso*amylamine (1 mol.) is added to solid primary *iso*amylamine hydrochloride (1 mol.). T. A. H.

Diamines. II. New Synthesis of Diamines. CARL NEUBERG [and ERNST NEIMANN] (*Zeit. physiol. Chem.*, 1905, **45**, 110—120. Compare this vol., i, 158, and Curtius and Clemm, Abstr., 1901, i, 68).—*Hexamethylenediamine* ($\alpha\zeta$-diaminohexane) is readily obtained when 1 to 3 grams of perfectly dry $\alpha\zeta$-diaminosuberic acid are distilled from a small flask. The platinichloride, aurichloride, and a *mercurichloride*, $C_6H_{16}N_2,2HCl,2HgCl_2$, have been prepared. *Octamethylenediamine* ($\alpha\theta$-diamino-octane), $NH_2\cdot[CH_2]_8\cdot NH_2$, obtained in a similar manner from diaminosebacic acid, yields precipitates with phosphotungstic acid, tannic acid, mercuric chloride, Nessler's reagent, or potassium bismuth iodide. Only an opalescence is produced with gold chloride or picric acid in dilute solution. The *mercurichloride* has the composition $C_8H_{20}N_2,2HgCl_2$. Lysine, when distilled, yields 7 per cent. of pentamethylenediamine, which was isolated in the form of its phenylcarbimide derivative. $\alpha\beta$-Diaminopropionic acid yields, in a similar manner, ethylenediamine. J. J. S.

Monamino-acids obtained from Seedlings of Vicia Sativa and Lupinus Albus. ERNST SCHULZE and ERNST WINTERSTEIN (*Zeit. physiol. Chem.*, 1905, **45**, 38—60. Compare Abstr., 1902, i, 595).—The cupric salts of glycine, alanine, leucine, phenylalanine, and of tyrosine are either insoluble or extremely sparingly soluble in cold methyl alcohol, whereas cupric aminovalerate dissolves with the greatest readiness in this solvent to a blue solution. At 18°, 1 gram dissolves in 52 grams of the alcohol. This affords a simple method

for the separation of aminovaleric acid from the amino-acids mentioned above, but not from Ehrlich's *iso*leucine (Abstr., 1904, i, 560).

The amino-acids formed in seedlings of *Vicia sativa* and of *Lupinus albus* have been isolated by E. Fischer's esterification method (Abstr., 1901, i, 192) after removal of leucine and *iso*leucine. From seedlings of *V. sativa* of 8—9 days' growth, only leucine, aminovaleric acid, *iso*leucine, and phenylalanine have been isolated. From etiolated seedlings of *Lupinus albus* of 18—20 days' growth, small quantities of 2-pyrrolidinecarboxylic acid in addition to aminovaleric acid, leucine, and phenylalanine have been isolated, and probably *iso*leucine is also present.

Tryptophan (Hopkins and Cole, Abstr., 1902, i, 193; 1903, i, 590) has also been isolated from the seedlings.

In seedlings 6 or 7 days old the amino-acid present in largest quantity is leucine, but in etiolated seedlings 2—3 weeks old the amount of this compared with aminovaleric acid and phenylalanine is comparatively small. J. J. S.

Amino-acid obtained by the Hydrolysis of the Proteids of Lupin Seeds. ERNST WINTERSTEIN and E. PANTANELLI (*Zeit. physiol. Chem.*, 1905, **45**, 61—68).—The proteids were prepared from the seeds by Ritthausen's method, hydrolysed with hydrochloric acid of sp. gr. 1·19, and the amino-acids separated by Fischer's method. The following have been isolated: alanine, aminovaleric acid, leucine, *iso*leucine, pyrrolidine-2-carboxylic acid, phenylalanine, aspartic acid, glutamic acid, and cystine. Tyrosine has been previously isolated by Schulze. J. J. S.

Synthesis of Hydroxy- and Diamino-acids. II. Diaminosuberic Acid and Diaminosebacic Acid. CARL NEUBERG [and ERNST NEIMANN] (*Zeit. physiol. Chem.*, 1905, **45**, 92—109. Compare this vol., i, 418).—Although diamino-derivatives of the lower members of the oxalic series of dibasic acids cannot readily be obtained by the action of ammonia on the corresponding dibromo-acids (Willstätter, *Ber.*, 1895, **28**, 657; 1902, **35**, 1379), $\alpha\zeta$-diaminosuberic acid and $\alpha\theta$-diaminosebacic acid are readily obtained by heating the dibromo-acids with concentrated aqueous ammonia and ammonium carbonate at 120°. *$\alpha\zeta$-Diaminosuberic acid*,

$$CO_2H\cdot CH(NH_2)\cdot[CH_2]_4\cdot CH(NH_2)\cdot CO_2H,$$

crystallises from hot ammonia, in which it is sparingly soluble, in glistening needles, and when heated above 300° sublimes and is partially decomposed into carbon dioxide and hexamethylenediamine. It dissolves in both alkalis and mineral acids. The *copper* and *silver* salts have been analysed. Precipitates are obtained when salts of most heavy metals are added to a solution of the sodium salt. The *hydrochloride*, $C_8H_{16}O_4N_2,2HCl$, is a crystalline mass, readily soluble in water, and the *phenylcarbimide* derivative, $C_{22}H_{26}O_6N_4$, crystallises from dilute alcohol in colourless needles melting at 250°.

$\alpha\theta$-Diaminosebacic acid, $CO_2H\cdot CH(NH_2)\cdot[CH_2]_6\cdot CH(NH_2)\cdot CO_2H$, crystallises in needles, decomposes above 300°, and closely resembles the diaminosuberic acid in all respects. The *phenylcarbimide* deriv-

ative melts at 210°. The *ethyl* ester distils at 240° under 10 mm. pressure, and forms a colourless oil soluble in water, alcohol, or ether, but insoluble in benzene or light petroleum; its aqueous solution has a distinct alkaline reaction and readily combines with two equivalents of acid. The *hydrochloride* crystallises in long needles soluble in water or alcohol, the *picrate*, $C_{26}H_{34}O_{18}N_8$, crystallises in sulphur-yellow needles which decompose at 198°.

The ester of diaminosuberic acid cannot be obtained by the usual method.

Both acids show a tendency to dissolve silica and alumina from porcelain vessels. J. J. S.

Synthesis of Polypeptides. XI. EMIL FISCHER (*Annalen*, 1905, **340**, 123—128. Compare Abstr., 1903, i, 465, 607, 799; 1904, i, 652, 771, 867, 890; this vol., i, 30, 31, 263, 637).—In continuation of the work which has been carried out during the last two years on the synthesis of polypeptides by the action of halogen acid chlorides on amino-acids, numerous other combinations have been examined in order to obtain, if possible, compounds which take part in the building up of proteids. In addition to the halogen acids previously employed, phenylbromoacetic acid has now been used.

The optically active polypeptides previously described were prepared from active amino-acids; by the use of racemic acid chlorides, a mixture of active products has now been obtained, which are separated by crystallisation. On the other hand, such optically active compounds have been prepared by using optically active acid chlorides; thus an optically active alanylglycine has been prepared, which is derived from the optical antipode of the natural alanine.

When melted, the polypeptides are converted into anhydrides, the diketopiperazines, each diketopiperazine corresponding with two polypeptides; thus, glycyl-leucine and leucylglycine yield the same anhydride, *iso*butyldiketopiperazine. K. J. P. O.

Synthesis of Polypeptides. XI. Alanylglycine and Leucylalanylglycine. EMIL FISCHER and WALTER AXHAUSEN (*Annalen*, 1905, **340**, 128—142).—In order to combine together the three amino-acid radicles in leucylalanylglycine, alanylglycine must first be prepared from glycine and α-bromopropionyl bromide, and then combined with α-bromohexoyl chloride; two isomeric substances are finally obtained.

α-Bromopropionylglycine, $CHBrMe\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, is prepared by treating a solution of glycine in sodium hydroxide with successive portions of bromopropionyl bromide and $N/1$ sodium hydroxide, and then evaporating the mixture to dryness under reduced pressure and extracting the residue several times with ether. The acid is precipitated with petroleum from the solution and crystallises from chloroform in aggregates of leaflets, which sinter at 100° and melt at 104° (corr.).

The *ethyl* ester of α-bromopropionylglycine,

$$CHBrMe\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et,$$

prepared from α-bromopropionyl bromide and glycine ethyl ester in ethereal solution, crystallises in lustrous, soft needles sintering at 53° and melting at 55·5° (corr.), and is readily hydrolysed by shaking with a cold dilute solution of sodium hydroxide.

Alanylglycine, $NH_2·CHMe·CO·NH·CH_2·CO_2H$, is prepared by heating bromopropionylglycine with excess of ammonia at 100°, evaporating the solution to dryness, and dissolving the dipeptide in 50 per cent. alcohol; it crystallises in needles melting and decomposing at 235° (corr.), and has a faint acid reaction. *Carbethoxyalanylglycine*, $CO_2Et·NH·CHMe·CO·NH·CH_2·CO_2H$, is prepared by shaking an alkaline solution of alanylglycine with ethyl chlorocarbonate and evaporating the solution to dryness after neutralising, and finally extracting with ethyl acetate; it crystallises in needles sintering at 117° and melting at 122° (corr.), and has a faint acid reaction.

*α-Bromo*iso*hexoylalanylglycine*,

$$CH_2Pr^{\beta}·CHBr·CO·NH·CHMe·CO·NH·CH_2·CO_2H,$$

is prepared by adding an excess of α-bromo*iso*hexoyl chloride to an alkaline solution of alanylglycine and extracting the oil with ether; the product, which is a mixture of two isomerides, crystallises from water in needles and has no sharp melting point. The isomeride with the higher melting point is obtained by extracting the solid with ether and recrystallising the insoluble part from ethyl acetate; it sinters at 150° and melts at 157° (corr.); the more soluble isomeride could not be obtained in a crystalline form.

The *leucylalanylglycine*,

$$CH_2Pr^{\beta}·CH(NH_2)·CO·NH·CHMe·CO·NH·CH_2·CO_2H,$$

prepared by the action of ammonia on the mixed bromo-compounds, is seen to consist under the microscope of two different forms, groups of needles and prisms. *Leucylalanylglycine* A is best obtained from the bromo*iso*hexoylalanylglycine melting at 154°, and melts and decomposes at 259° (corr.); it has a faint acid reaction, and is soluble in alkalis and acids. *Leucylalanylglycine* B, prepared from the amorphous bromohexoylalanylglycine, crystallises in thick prisms melting at 233° (corr.), but in other properties resembles the tripeptide A. The benzoyl derivative of leucylalanylglycine A is prepared by treatment of an aqueous solution of the tripeptide with benzoyl chloride in the presence of sodium hydrogen carbonate, and crystallises with H_2O in four sided plates or leaflets, losing water at 100° and melting at 194·5—195·5° (corr.). The *benzoyl-leucylalanylglycine* B crystallises from water in anhydrous, colourless needles melting at 209—210°.

Carbethoxyalanine, $CO_2Et·NH·CHMe·CO_2H$, crystallises in colourless leaflets melting at 84° (corr.); its *ethyl* ester, prepared from the ethyl ester of alanine and ethyl chlorocarbonate, crystallises in long needles melting at 25° (corr.), and is hydrolysed by shaking with a cold dilute solution of sodium hydroxide, carbethoxylalanine being formed. *Carbethoxyalanineamide*, $CO_2Et·NH·CHMe·CO·NH_2$, prepared from the corresponding ester by heating with a saturated alcoholic solution of ammonia and extracting the solid left after evaporation with ethyl acetate, crystallises in short needles melting at 120—121° (corr.). *Carbethoxyalanine chloride*, prepared from carbethoxyalanine and thionyl chloride, is unstable; dissolved in dry ether, it reacts with the

ethyl ester of glycine, yielding *carbethoxyalanylglycine ethyl* ester, $CO_2Et \cdot NH \cdot CHMe \cdot CO \cdot NH \cdot CH_2 \cdot CO_2Et$, which crystallises in needles melting at 67·5° (corr.), and is readily hydrolysed by alkalis. The corresponding *amide*, prepared from the ester by the action of ammonia, crystallises in needles sintering at 114° and melting at 119° (corr.).

K. J. P. O.

Synthesis of Polypeptides. XI. Leucylglycine and Alanylleucylglycine. EMIL FISCHER and ARNOLD BRUNNER (*Annalen*, 1905, **340**, 142—151).—*a-Bromo*iso*hexoylglycine*,

$$CH_2Pr^{\beta} \cdot CHBr \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H,$$

is prepared by shaking an alkaline solution of glycine with a-bromo*iso*hexoyl chloride, and purified by crystallisation from water; it melts at 135° (corr.). When treated with aqueous ammonia, *leucylglycine* is obtained in six-sided plates melting and decomposing at 243° (corr.), and having a faint acid reaction. It forms an insoluble, deep blue, crystalline *copper* salt, $(C_8H_{15}O_3N_2Cu)_2O,H_2O$, which loses water under reduced pressure at 80°.

The *anhydride* of leucylglycine, *diketo*iso*butylpiperazine*,

$$CH_2Pr^{\beta} \cdot CH<\begin{matrix} NH \cdot CO \\ CO \cdot NH \end{matrix}>CH_2,$$

prepared by heating the dipeptide at 235—240°, crystallises in large prisms melting at 245° (corr.), and is identical with the substance obtained by heating the ethyl ester of leucylglycine with alcoholic ammonia.

Carbethoxyleucylglycine,

$$CH_2Pr^{\beta} \cdot CH(NH \cdot CO_2Et) \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H,$$

prepared from leucylglycine and ethyl chlorocarbonate, crystallises in microscopic needles sintering at 123° and melting at 127° (corr.). *Benzoyl-leucylglycine*, $CH_2Pr^{\beta} \cdot CH(NH \cdot COPh) \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$, forms very long needles melting at 167° (corr.).

a-Bromopropionyl-leucylglycine, prepared from leucylglycine and a-bromopropionyl bromide, crystallises from water in anhydrous needles melting and decomposing at 165° (corr.). On keeping in contact with aqueous ammonia, the tripeptide, *alanyl-leucylglycine*, $NH_2 \cdot CHMe \cdot CO \cdot NH \cdot CH(CH_2Pr^{\beta}) \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$, is obtained in concentric groups of needles melting and decomposing at 232° (corr.), and has a faintly acid reaction.

K. J. P. O.

Synthesis of Polypeptides. XI. Glycyl-leucine, Alanylleucine, Leucylalanine, Glycylalanyl-leucine, and Active Alanylglycine. EMIL FISCHER and OTTO WARBURG (*Annalen*, 1905, **340**, 152—167).—*a-Bromopropionyl-leucine*,

$$CHMeBr \cdot CO \cdot NH \cdot CH(CH_2Pr^{\beta}) \cdot CO_2H,$$

prepared from leucine and bromopropionyl bromide, is a mixture of two isomerides, melting at 105—135°, which are separated by fractional crystallisation from water; the less soluble, *a-bromopropionylleucine* A, forms 10 per cent. of the crude product, and crystallises in microscopic plates melting at 147—150° (corr.). *a-Bromopropionylleucine* B, which forms 50 per cent. of the crude product, melts at 113—118° (corr.).

Alanyl-leucine A, $NH_2 \cdot CHMe \cdot CO \cdot NH \cdot CH(CH_2Pr^{\beta}) \cdot CO_2H$, prepared from the corresponding bromopropionyl-leucine, crystallises from water in four-sided plates melting and decomposing at 248° (corr.). With phenylcarbimide, it yields a *phenylcarbamide*, which crystallises in plates melting and decomposing at 214—218° (corr.). *Alanyl-leucine* B resembles its isomeride very closely, but crystallises in needles; the *phenylcarbamide* crystallises in needles melting at 185—189° (corr.).

Chloroacetyl-leucine, $CH_2Cl \cdot CO \cdot NH \cdot CH(CH_2Pr^{\beta}) \cdot CO_2H$, prepared from leucine and chloroacetyl chloride in alkaline solution, crystallises in rhombic plates melting at 142° (corr.). When treated with ammonia, it is converted into *glycyl-leucine*,

$$NH_2 \cdot CH_2 \cdot CO \cdot NH \cdot CH(CH_2Pr^{\beta}) \cdot CO_2H,$$

which crystallises in microscopic leaflets melting and decomposing at 242°, and gives a characteristic insoluble blue precipitate with copper sulphate, but not with other copper salts. When heated to its melting point, the dipeptide yields an anhydride which is identical with the compound obtained from leucylglycine (Fischer and Brunner, this vol., i, 690).

*a-Bromo*iso*hexoylalanine*, $CH_2Pr^{\beta} \cdot CHBr \cdot CO \cdot NH \cdot CHMe \cdot CO_2H$, is obtained unmixed with an isomeride, crystallising in colourless leaflets melting at 123—126°, and is converted into *leucylalanine*,

$$CH_2Pr^{\beta} \cdot CH(NH_2) \cdot CO \cdot NH \cdot CHMe \cdot CO_2H,$$

by treatment with ammonia; the dipeptide crystallises in small plates melting and decomposing at 248° (corr.), and has a faint acid reaction. In the formation of this dipeptide two by-products are obtained; the one is probably the *anhydride* of leucylalanine, and the other iso-*hexenoylalanine*, which would be produced by elimination of hydrogen bromide from the bromohexoyl derivative. It is isolated as a strongly acid oil, which, when heated with dilute sulphuric acid, gives an oily volatile acid resembling *a-iso*hexenoic acid.

Carbethoxyleucylalanine,

$$CO_2Et \cdot NH \cdot CH(CH_2Pr^{\beta}) \cdot CO \cdot NH \cdot CHMe \cdot CO_2H,$$

crystallises in four-sided plates melting at 166—168° (corr.). *Leucylalanine anhydride* (*diketomethyl*iso*butylpiperazine*),

$$CH_2Pr^{\beta} \cdot CH{<}{\substack{NH \cdot CO \\ CO \cdot NH}}{>}CHMe,$$

prepared by heating leucylalanine at 250°, crystallises in needles melting at 247° (corr.). *Chloroacetyl-leucylalanine*,

$$CH_2Cl \cdot CO \cdot NH \cdot CH(CH_2Pr^{\beta}) \cdot CO \cdot NH \cdot CHMe \cdot CO_2H,$$

prepared from leucylalanine and chloroacetyl chloride, melts indistinctly at 158—161° (corr.).

Glycyl-leucylalanine,

$$NH_2 \cdot CH_2 \cdot CO \cdot NH \cdot CH(CH_2Pr^{\beta}) \cdot CO \cdot NH \cdot CHMe \cdot CO_2H,$$

crystallises in four-sided plates melting and decomposing at 250° (corr.), reddens blue litmus paper, and gives a reddish-violet coloration with alkali and a copper salt.

l-*Alanylglycine*, $NH_2 \cdot CHMe \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$, was prepared by means of *l*-bromopropionyl chloride and the ethyl ester of glycine; the *ethyl* ester of l-*bromopropionylglycine* thus obtained melts at 50—52°, and on hydrolysis yields l-*bromopropionylglycine*, which melts 20° higher than the inactive isomeride. The dipeptide is obtained by

treating the bromopropionylglycine with aqueous ammonia at the ordinary temperature, and crystallises in tetrahedra melting and decomposing at 256° (corr.). It has in aqueous solution $[\alpha]_D -48.6°$ at 20°; a small quantity of the racemic compound may be mixed with the dipeptide, but on hydrolysis with concentrated hydrochloric acid the theoretical quantity of active alanine is found.

K. J. P. O.

Synthesis of Polypeptides. XI. Optically Active α-Bromopropionic Acid. EMIL FISCHER and OTTO WARBURG (*Annalen*, 1905, **340**, 168—172).—Cinchonine, strychnine, and brucine can all be used in order to separate inactive bromopropionic acid into its active constituents; in the case of brucine the dextrorotatory acid, and in the case of strychnine the lævorotatory acid, crystallises out first. *l*-Bromopropionic acid is obtained by repeated recrystallisation (15—20 times) of the cinchonine bromopropionate from water. The salt is then dissolved in dilute hydrochloric acid, and the *l*-bromopropionic acid extracted with ether and distilled under a pressure of 0·2—0·4 mm., when it boils at 70—80°. The pure acid is an oil of sp. gr. 1·7084 and $[\alpha]_D -26.7°$ at 20°. By prolonged treatment with 25 per cent. ammonia, it is converted into *l*-alanine, which has $[\alpha]_D -9°$.

l-*Bromopropionyl chloride*, prepared by the action of thionyl chloride on the acid at 55—65°, boils at 27° under 12 mm. pressure. *l*-Bromopropionic acid is prepared from *d*-alanine by treatment with bromine and potassium bromide in the presence of dilute sulphuric acid and passing in nitrous fumes for several hours (Walden's method). The excess of bromine is removed and the bromopropionic acid distilled under reduced pressure.

K. J. P. O.

Synthesis of Polypeptides. XI. Leucyl*iso*serine. EMIL FISCHER and WILHELM F. KOELKER (*Annalen*, 1905, **340**, 172—180).—*α-Bromo*iso*hexoyl*iso*serine*, $CH_2Pr^{\beta}\cdot CHBr\cdot CO\cdot NH\cdot CH_2\cdot CH(OH)\cdot CO_2H$, prepared from *iso*serine and α-bromo*iso*hexoyl chloride, crystallises in six-sided plates melting at 136—139° (corr.), and is probably a mixture, since, when treated with ammonia, it yields a mixture of two leucyl*iso*serines, which are separated by fractional crystallisation from water. *Leucyl*iso*serine* A, $CH_2Pr^{\beta}\cdot CH(NH_2)\cdot CO\cdot NH\cdot CH_2\cdot CH(OH)\cdot CO_2H$, is sparingly soluble in water and crystallises in microscopic plates (with H_2O), melting and decomposing at 228°; it has a faintly acid reaction and dissolves copper oxide. The *phenylcarbamide*,

$NHPh\cdot CO\cdot NH\cdot CH(CH_2Pr^{\beta})\cdot CO\cdot NH\cdot CH_2\cdot CH(OH)\cdot CO_2H$,

crystallises in prisms melting at 176—177° (corr.).

*Leucyl*iso*serine* B crystallises in readily soluble anhydrous needles melting and decomposing at 234° (corr.); the *phenylcarbamide* forms prisms melting at 192—193° (corr.).

Both the isomeric dipeptides, when hydrolysed with hydrochloric acid, behave in exactly the same way, yielding a mixture of leucine and *iso*serine.

If the two leucyl*iso*serines are structurally isomeric, in the sense of the formulæ $CH_2Pr^{\beta}\cdot CH(NH_2)\cdot CO\cdot O\cdot CH(CH_2\cdot NH_2)\cdot CO_2H$ and $CH_2Pr^{\beta}\cdot CH(NH_2)\cdot CO\cdot NH\cdot CH_2\cdot CH(OH)\cdot CO_2H$, their reaction with

nitrous acid should be different owing to the different number of NH_2 groups. It was found that the behaviour of the two dipeptides was identical, but it was also ascertained that nitrous acid, at least in the case of dipeptides, does not sharply distinguish between amino- and imino-groups; both are attacked with the evolution of nitrogen. Experiments were carried out with α-bromo*iso*hexoyl*iso*serine and with hippuric acid and hippuryl*iso*serine; the results with the compound last mentioned do not agree with Curtius' conclusion (Abstr., 1904, i, 886) that the hippuryl group is linked with oxygen. The compound has no basic properties and therefore contains no amino-group; its formula is probably $NHBz\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CH(OH)\cdot CO_2H$. K. J. P. O.

Synthesis of Polypeptides. XI. Derivatives of α-Aminobutyric Acid. EMIL FISCHER and KARL RASKE (*Annalen*, 1905, **340**, 180—190).—Although α-aminobutyric acid has not hitherto been observed among the decomposition products of natural proteids, it is so nearly related to alanine and aminovaleric acid that the polypeptides derived from it have been studied.

α-Bromobutyryl chloride, $CHBrEt\cdot COCl$, prepared from α-bromobutyric acid and phosphorus pentachloride, is a heavy liquid of unpleasant odour boiling at 43° under 25 mm. pressure, and combines with glycine giving *α-bromobutyrylglycine*, $CHBrEt\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, which is a crystalline solid and melts at 101—105° (corr.). The bromo-derivative is converted by aqueous ammonia into *α-aminobutyrylglycine*, which is a crystalline powder becoming brown at 200° and melting at 220° (corr.), when it changes with elimination of water into the *anhydride*, $CHEt<\begin{matrix}CO\cdot NH\\NH\cdot CO\end{matrix}>CH_2$, *diketoethylpiperazine*; the latter crystallises in rhombic plates melting at 237—239° (corr.) and shows no basic properties.

When α-aminobutyric acid and α-bromobutyryl chloride are caused to interact, two isomeric *α-bromobutyryl-α-aminobutyric acids*, $CHBrEt\cdot CO\cdot NH\cdot CHEt\cdot CO_2H$, which differ in solubility, are formed. The less soluble, the A compound, crystallises from water in small needles melting at 133° (corr.), whilst the B compound, which contributes the major quantity of the mixture, forms crystals melting at 95° (corr.).

α-Aminobutyryl-α-aminobutyric acid A, prepared from the corresponding bromo-compound, crystallises in leaflets, becoming brown at 260° and melting at 273° (corr.); it has the usual faintly acid properties; the *copper* salt is crystalline and sparingly soluble. The B *compound*, prepared from the B bromo-derivative, crystallises in microscopic needles and prisms becoming brown at 240° and melting at 257° (corr.); its soluble *copper* salt crystallises in microscopic prisms.

α-Aminobutyric anhydride (*diketodiethylpiperazine*),

$$CHEt<\begin{matrix}CO\cdot NH\\NH\cdot CO\end{matrix}>CHEt,$$

is obtained by heating both the isomeric dipeptides above their melting points and forms a crystalline mass melting at 267°; its behaviour towards dilute acids is neutral. K. J. P. O.

Synthesis of Polypeptides. XI. Dipeptides of Phenylglycine with Glycine, Alanine, Asparagine, and Aspartic Acid. EMIL FISCHER and JULIUS SCHMIDLIN (*Annalen*, 1905, **340**, 190—204).—The phenylbromoacetic acid required for the preparation of those dipeptides which contain phenylglycine is prepared by the action of phosphorus pentabromide on mandelic acid and treatment of the resulting acid bromide with water. *Phenylbromoacetyl chloride*, CHBrPh·COCl, prepared from the corresponding acid and phosphorus pentachloride, is a liquid boiling at 117—118° under 18 mm. pressure; it combines with glycine yielding *phenylbromoacetylglycine*,

$$CHBrPh\cdot CO\cdot NH\cdot CH_2\cdot CO_2H,$$

which crystallises in needles melting at 106—109° (corr.). On treatment with ammonia, the latter gives *phenylglycylglycine*,

$$NH_2\cdot CHPh\cdot CO\cdot NH\cdot CH_2\cdot CO_2H,$$

crystallising in leaflets melting and decomposing at 248° (corr.); its *copper* salt, $C_{10}H_{10}O_3N_2Cu$, crystallises in pale blue leaflets.

Phenylglycylglycine anhydride (*diketophenylpiperazine*),

$$CHPh{<}{\substack{CO\cdot NH\\ NH\cdot CO}}{>}CH_2,$$

prepared by heating the dipeptide above its melting point, or, better, by heating the ester of phenylglycylglycine with alcoholic ammonia, crystallises in aggregates of long needles melting and becoming coloured at 240° (corr.).

Phenylbromoacetylalanine, $CHBrPh\cdot CO\cdot NH\cdot CHMe\cdot CO_2H$, prepared from alanine and phenylacetyl chloride, exists in two isomeric forms, which are separated by fractional crystallisation from ethyl acetate. The A compound is the less soluble in ethyl acetate and crystallises in needles melting at 170—171° (corr.); the B compound crystallises in short needles melting at 148—151° (corr.). *Phenylhydroxyacetylalanine*, $OH\cdot CHPh\cdot CO\cdot NH\cdot CHMe\cdot CO_2H$, is obtained by boiling both the isomeric bromo-compounds with water and crystallises in aggregates of needles melting at 142—145° (corr.). *Phenylglycinealanine* A, $NH_2\cdot CHPh\cdot CO\cdot NH\cdot CHMe\cdot CO_2H$, is prepared from the corresponding bromo-compound and crystallises in leaflets melting and decomposing at 249°; the B *compound* is very sparingly soluble in water and crystallises in leaflets melting at 239° (corr.).

Phenylbromoacetylasparagine,

$$CHBrPh\cdot CO\cdot NH\cdot CH(CO\cdot NH_2)\cdot CH_2\cdot CO_2H,$$

prepared from *l*-asparagine and phenylbromoacetyl chloride, crystallises in needles melting at 163—164° (corr.), and has, in alkaline solution, $[\alpha]_D$ +3·33° at 20°; the material did not appear to consist of two isomerides, as was expected. Prolonged treatment with ammonia converts the substance last mentioned into *phenylglycineasparagine*, $NH_2\cdot CHPh\cdot CO\cdot NH\cdot CH(CO\cdot NH_2)\cdot CH_2\cdot CO_2H$, which crystallises in short prisms melting at 237° (corr.) and having $[\alpha]_D$ −2·3° at 20° in alkaline solution.

Phenylbromoacetylaspartic acid,

$$CHBrPh\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H,$$

prepared from *l*-aspartic acid and phenylbromoacetyl chloride, is crystalline and melts at 139—143°, and has $[\alpha]_D$ +3·6° at 20°. With ammonia, a *compound* melting at 201° is obtained, which seems to be

an impure dipeptide. The *diethyl* ester, prepared from phenylbromoacetyl chloride and ethyl aspartate, exists only in one form, which crystallises in long needles melting at 70—71° (corr.) and has $[\alpha]_D$ $-13{\cdot}23°$ at 20°.

The *anhydride* of phenylglycylasparagine,

$$CHPh{<}{}^{CO\cdot NH}_{NH\cdot CO}{>}CH\cdot CH_2\cdot CO\cdot NH_2,$$

is prepared by heating the ester just described with a solution of ammonia in methyl alcohol; it crystallises in long prisms melting at 271° (corr.) and is easily decomposed by warm dilute sodium hydroxide. K. J. P. O.

Action of Phosphorus Pentasulphide on Carbamide and Thiocarbamide. Franz von Hemmelmayer (*Monatsh.*, 1905, **26**, 765—782).—Contrary to Kutschig's statement (Abstr., 1888, 1064), the product of the interaction of phosphorus pentasulphide and carbamide is *ammonium thiobiuretphosphate*, $NH{<}{}^{CO\cdot NH}_{CO\cdot NH}{>}PS\cdot SNH_4$, which crystallises in monoclinic plates, decomposes at 252°, has an acid reaction in aqueous solution, evolves ammonia when heated with potassium hydroxide, gives no precipitation with magnesia mixture, and when boiled with dilute hydrochloric acid, in air or in an atmosphere of carbon dioxide, is decomposed into hydrogen sulphide, biuret, and phosphoric acid. On adding ammonia and alcohol to the aqueous solution of the primary ammonium salt, an *ammonium* salt is obtained which crystallises in glistening prisms, and on exposure to the air decomposes into ammonia and the original ammonium salt; with barium chloride in aqueous solution, the tertiary *barium* salt, $(C_2H_3O_3N_3S_2P)_2Ba_3,8\frac{1}{2}H_2O$, is obtained in glistening leaflets; it loses part of its water of crystallisation in a desiccator, has a strong alkaline reaction, and is oxidised by concentrated nitric acid or by bromine water in hydrochloric acid solution; this salt is derived from the acid $NH{<}{}^{CO\cdot NH}_{CO\cdot NH}{>}P(SH)_2\cdot OH$.

Thiobiuretphosphoric acid, $NH{<}{}^{CO\cdot NH}_{CO\cdot NH}{>}PS\cdot SH,2H_2O$, is obtained by treating the tertiary barium salt with sulphuric acid. It forms colourless, crystalline crusts, commences to decompose at 78°, changes to an opaque, white mass in a desiccator, has a strong acid reaction, and with aqueous ammonia yields the primary ammonium salt. If thiocarbamide and phosphorus pentasulphide are heated together at 130° and the product treated with water, an oil is obtained which slowly solidifies to crystals melting at about 118°; the aqueous solution contains phosphoric acid and ammonium thiocyanate. If the mixture is heated at 160°, the products are ammonium phosphate and thiocyanate and a small amount of a substance which forms large, yellow crystals and melts at 186°. G. Y.

Mercuric Zinc Cyanide. David B. Dott (*Pharm. J.*, 1905, [iv], 21, 136—137).—It has been stated by Dunstan (Trans., 1892, 61,

666) that mercuric zinc cyanide, obtained by mixing solutions of mercuric cyanide, potassium cyanide, and zinc sulphate, consists of a double salt, $Zn_4Hg(CN)_{10}$, mixed with a varying proportion of zinc cyanide.

From an investigation of this precipitate, it is concluded that it has no definite composition and that the cyanide having the above formula does not exist. It is suggested that the product is a loose molecular or merely physical combination and should be termed simply "zinc and mercury cyanide." E. G.

Cyanide Mud. ADOLF HAND (*Zeit. angew. Chem.*, 1905, **18**, 1098—1106).—The "cyanide mud" obtained in the recovery of cyanogen compounds from coal-gas according to Bueb's process (D.R.-P. 112459) consists of the insoluble compound,

$$2NH_4CN,Fe(CN)_2,$$

and ammonium ferrocyanide. Ammonia may be readily recovered from it. A. McK.

Compounds of Hydrogen Chloride, Hydrocarbons, and Aluminium Chloride Ferments which are formed in Friedel and Craft's Synthesis of Benzene Homologues. GABRIEL GUSTAVSON (*J. pr. Chem.*, 1905, [ii], **72**, 57—79. Compare Abstr., 1903, i, 470, 804; this vol., i, 334).—The compound

$$Al_2Cl_6,2C_6H_3Pr^{\beta}_3,HCl$$

is formed by mixing aluminium chloride, benzene, and *iso*propyl chloride in any order. The reaction takes place in two stages: on adding drop by drop a mixture of 2 mols. of benzene and 3 mols. of *iso*propyl chloride to aluminium chloride at 0°, the green liquid *compound*, $Al_2Cl_6,C_6H_3Pr^{\beta}_3,C_6H_6$, is formed. This unites with 5 mols. of benzene to form the compound $Al_2Cl_6,C_6H_3Pr^{\beta}_3,6C_6H_6$, yields $Al_2Cl_6,C_6H_3Pr^{\beta}_3$ when washed with light petroleum, is decomposed by water with formation of benzene and tri*iso*propylbenzene, and reacts with *iso*propyl chloride at −10° to form the compound

$$Al_2Cl_6,2C_6H_3Pr^{\beta}_3,HCl.$$

When heated in a closed vessel at 65—70°, this melts and dissociates into the ferment $Al_2Cl_6,C_6H_3Pr^{\beta}_3$, tri*iso*propylbenzene and hydrogen chloride: these form two layers, and recombine on cooling and shaking. If the hydrogen chloride is allowed to escape at 65—70°, the two layers do not recombine, except after treatment with hydrogen chloride at −10°.

The tri*iso*propylbenzene yields trimesic acid when oxidised with dilute nitric acid at 190—200°, and is therefore *s*-tri*iso*propylbenzene.

The *sulphonic acid* crystallises in needles and is only sparingly soluble in water; the *barium* ($+6H_2O$), *sodium* ($+6H_2O$), and magnesium ($+7H_2O$) salts are described.

In comparison with the ethyl ferment, $Al_2Cl_6,C_6H_3Et_3$, the *iso*propyl ferment is unstable, decomposing slowly at the laboratory temperature, rapidly at 100° with evolution of a saturated gaseous hydrocarbon and the formation of a viscid, orange liquid, which, on treat-

ment with water, yields hydrocarbons which rapidly become resinous, but not tri*iso*propylbenzene.

The compound $Al_2Cl_6,2C_6H_3Pr^{\beta}_3,HCl$ is formed also by the action of *s*-tri*iso*propylbenzene and hydrogen chloride on the compound $Al_2Cl_6,C_6H_3Pr^{\beta}_3,C_6H_6$ at $-10°$, or of di*iso*propylbenzene and *iso*propyl chloride on the ferment $Al_2Cl_6,C_6H_3Pr^{\beta}_3$, or of hydrogen chloride and tri*iso*propylbenzene on aluminium chloride in presence of a small quantity of benzene. When shaken with an excess of benzene, it forms the compound $Al_2Cl_6,C_6H_3Pr^{\beta}_3,6C_6H_6$, hydrogen chloride and *s*-tri*iso*propylbenzene, the greater part of which under the influence of the ferment reacts with the excess of benzene to form *iso*propylbenzene.

If a current of hydrogen chloride is passed through a mixture of 1 mol. of aluminium chloride and 2 mols. of *s*-triethylbenzene, the *compound* $Al_2Cl_6,2C_6H_3Et_3,HCl$ is formed as a yellow, crystalline mass, which is also obtained by passing hydrogen chloride through a mixture of the ethyl ferment, $Al_2Cl_6,C_6H_3Et_3$, and *s*-triethylbenzene at $-8°$. It melts and evolves hydrogen chloride at 50°, and when shaken with benzene dissolves with formation of two layers, the lower of which, when washed with light petroleum, yields the ethyl ferment.

The *compound* $Al_2Cl_6,C_6H_3Et_3,C_6H_3Pr^{\beta}_3,HCl$ is formed by the action of hydrogen chloride on a mixture of the ethyl ferment,

$$Al_2Cl_6,C_6H_3Et_3,$$

and *s*-tri*iso*propylbenzene at $-10°$, or of *iso*propyl chloride on the compound $Al_2Cl_6,C_6H_3Et_3,C_6H_6$.

The action of *tert.*-butyl chloride and benzene on aluminium chloride at $-10°$ leads to the formation of a yellow, crystalline compound, which is formed also by the action of *p*-di-*tert.*-butylbenzene and *tert.*-butyl chloride on powdered aluminium chloride at $-10°$.

tert.-Amyl chloride, benzene, and aluminium chloride react at $-8°$ to form a liquid compound, which is formed also by the action of hydrogen chloride on a mixture of 1 mol. of aluminium chloride and 2 mols. of di-*tert.*-amylbenzene. This decomposes at the ordinary temperature with evolution of a gaseous, saturated hydrocarbon.

G. Y.

Oxidation of Aromatic Hydrocarbons by means of Cerium Peroxide. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 158609).—Cerium peroxide is found to behave as a powerful oxidising agent, comparable with chromic acid, towards organic compounds in the presence of dilute acids. The crude cerium peroxide containing didymium, obtained in the manufacture of incandescent gas mantles, is suitable for the purpose. It forms a brown powder, insoluble in dilute acids, but dissolving readily in presence of aromatic hydrocarbons. Thus toluene is oxidised at 90° in 60 per cent. sulphuric acid, giving a 33 per cent. yield of benzaldehyde, together with small quantities of tolylphenylmethane and anthraquinone. Anthracene yields anthraquinone; naphthalene yields naphthaquinone or phthalic acid, according to the proportion of cerium peroxide employed. In

presence of sulphuric acid, the reaction may be so violent as to cause charring. C. H. D.

Constitution of *as*-Di-*p*-tolylethane, 2 : 7 : 9 : 10-Tetramethylanthracene Dihydride, and 2 : 7-Dimethylanthracene. JAMES LAVAUX (*Compt. rend.*, 1905, **141**, 354—356).—The ditolylethane obtained by Anschütz and Romig by condensing toluene with ethylidene chloride in presence of aluminium chloride (Abstr., 1885, 768) is di-*p*-tolylethane, since it is identical with Fischer's hydrocarbon (Abstr., 1875, 154), which on oxidation yields Weiler's ditolyl ketone (Abstr., 1875, 151), and this was shown to be *p*-ditolyl ketone by Ador and Crafts (Abstr., 1878, 405). Assuming that the tetramethylanthracene dihydride, simultaneously obtained by Anschütz and Romig, is produced by the further action of 1 mol. of ethylidene chloride on 1 mol. of this di-*p*-tolylethane (compare this vol., i, 43, for a similar reaction), then it can only be the 2 : 7 : 9 : 10-tetramethylanthracene dihydride, and the product obtained by the oxidation of the latter with chromic acid (Anschütz and Romig, *loc. cit.*) must be 2 : 7-dimethylanthraquinone. The latter is also produced by the oxidation of the B-dimethylanthracene obtained by the author (this vol., i, 125); therefore this B-hydrocarbon must be 2 : 7-dimethylanthracene, and is identical with that also obtained by Anschütz and Romig by distilling the tetramethylanthracene hydride, already referred to, with zinc dust. T. A. H.

Pyrogallol 1 : 3-Dimethyl Ether and 2 : 6-Dimethoxybenzoquinone. CARL GRAEBE and HANS HESS (*Annalen*, 1905, **340**, 232—243).—The partial methylation of pyrogallol by means of methyl sulphate leads, when molecular proportions of the phenol and the alkali hydroxide are used, to a mixture of the monomethyl and dimethyl ethers with unchanged pyrogallol. The same result is obtained when methyl iodide is used.

Pyrogallol 1 : 3-dimethyl ether, $C_6H_3(OMe)_2{\cdot}OH$ [OMe : OH : OMe = 1 : 2 : 3], could not be prepared in a pure state from pyrogallol, but only by heating syringic acid at 240—270°; it forms crystals melting at 54·8° and boiling at 262·7°; the picrate crystallises in orange-yellow needles melting at 61°. The *acetyl* derivative, $C_8H_9O_2{\cdot}OAc$, forms crystals melting at 53·5°. When oxidised with sodium nitrite in acid solution, the dimethyl ether is converted into cedriret.

2 : 6-Dimethoxybenzoquinone, $C_6H_2O_2(OMe)_2$, is best prepared by oxidising the trimethyl ether of pyrogallol with nitric acid of sp. gr. 1·2 in alcoholic solution; it melts at 255°. When treated with chlorine in chloroform solution, it is converted into 3 : 5-*dichloro*-2 : 6-*dimethoxybenzoquinone*, $C_8H_6O_4Cl_2$, which forms red crystals melting at 159°, and is identical with the β-ether obtained by Kehrmann (Abstr., 1889, 707; 1890, 136, and 1891, 903) by boiling chloroanil with methyl-alcoholic potassium hydroxide. When boiled with methyl-alcoholic alkali hydroxide, *chloromethoxydihydroxybenzoquinone*, $C_6ClO_2(OH_2){\cdot}OMe$, is obtained as red needles melting at 203°; the corresponding chloroethoxydihydroxybenzoquinone, which was prepared by Kehrmann,

is formed when alcoholic potassium hydroxide is used. 3-*Chlorodimethoxybenzoquinone*, $C_8H_7O_4Cl$, is formed in the partial chlorination of dimethoxybenzoquinone in chloroform, and consists of reddish-yellow crystals melting at 148°. K. J. P. O.

Chloronium Salts. JULIUS STIEGLITZ and EDITH E. BARNARD (*J. Amer. Chem. Soc.*, 1905, **27**, 1016—1019).—Baeyer (this vol., i, 281) has described some intensely coloured salts of *p*-trichloro- and *p*-tri-iodo-triphenylcarbinol, and has concluded that these substances do not have the quinonoid structure, for example, $C(C_6H_4Cl)_2:C_6H_4Cl{\cdot}O{\cdot}SO_3H$, but have the constitution of carbonium salts, $C(C_6H_4Cl)_3{\cdot}O{\cdot}SO_3H$.

It is suggested that these compounds may be chloronium salts of the structure $C(C_6H_4Cl)_2:C_6H_4:Cl{\cdot}O{\cdot}SO_3H$, and evidence is brought forward in support of this view. The opinion is expressed that the existence of true carbonium salts remains very doubtful, and that the quinonoid constitution should still be adopted for the triphenylmethane dyes. E. G.

Formation of Aromatic Methoxy-acids and of Anisole. CARL GRAEBE (*Annalen*, 1905, **340**, 204—212).—It has generally been stated that in methylation by means of methyl sulphate only one of the methyl groups is actually used, but it has been found that 1 mol. of methyl sulphate will methylate 2 mols. of phenol. The methylation takes place in two stages, the first methyl group entering rapidly in the cold, whilst the introduction of the second group occurs only slowly and at a high temperature. In the methylation of hydroxybenzoic acids, it has been found that the hydroxyl groups in the meta- and para-positions are far more readily converted into methoxyl groups than the hydroxyl group in the ortho-position relative to the carboxyl group. The same rule holds good when the methylation is effected by methyl iodide. If a mixture of *o*- and *p*- or of *o*- and *m*-hydroxybenzoic acids is treated with methyl sulphate, the meta- and para-acids are first methylated whilst the salicylic acid remains unchanged. A mixture of meta- and para-acids yields equal amounts of methyl derivative in a given time.

The methylation is best carried out by shaking a faintly alkaline aqueous solution of the phenol or hydroxy-compound with the methyl sulphate, and then adding excess of alkali and boiling.

K. J. P. O.

Specific Rotatory Powers of Tyrosine Preparations of Vegetable Origin. ERNST SCHULZE and ERNST WINTERSTEIN (*Zeit. physiol. Chem.*, 1905, **45**, 79—83. Compare Abstr., 1902, i, 595).—The following values of $[\alpha]_D$ at 20° for tyrosine prepared from various sources have been obtained. From potato $-14{\cdot}6°$ to $-16{\cdot}1°$; from tubers of *Dahlia variabilis* $-12{\cdot}9°$; by autolysis of seedlings of *Lupinus albus* $-16{\cdot}2°$. Fischer has previously (Abstr., 1900, i, 172) found for tyrosine from casein $-11{\cdot}6$ to $-13{\cdot}2°$, and for a product obtained by the resolution of racemic tyrosine a value $+16{\cdot}4°$. The differences are attributed to the presence of small amounts of the

racemic compound in some of the specimens obtained from natural sources. All determinations were made in 4 per cent. hydrochloric acid solution. J. J. S.

Reaction between Unsaturated Compounds and Organic Magnesium Compounds. VI. Reactions with Ethyl Benzylidenemalonate. ELMER P. KOHLER (*Amer. Chem. J.*, 1905, **34**, 132—147).—In studying the reactions between ethyl benzylidenemalonate and organic magnesium compounds, the following general method was adopted. An ethereal solution of the ester (1 mol.) was added gradually to a well-cooled solution of the magnesium compound (1 mol.), and the mixture was boiled for half an hour. The magnesium derivatives were not isolated. The esters obtained by decomposing the magnesium derivatives are easily hydrolysed, and give a good yield of the corresponding acids.

Ethyl diphenylmethylmalonate, $CHPh_2\cdot CH(CO_2Et)_2$, obtained by the action of magnesium phenyl bromide on ethyl benzylidenemalonate, boils at 235—250° under 12 mm. pressure, crystallises in slender needles, melts at 63°, and is readily soluble in alcohol, ether, or carbon disulphide; the *sodium* derivative forms small, white needles. *Ethyl hydrogen diphenylmethylmalonate* crystallises in thick needles, melts at 165—166°, decomposes above 220°, and is readily soluble in ether or acetone. *Diphenylmethylmalonic acid* crystallises from water in thin plates, and from alcohol in needles, melts and decomposes at 190—192°, and is easily soluble in alcohol or ether, and moderately so in hot water; it is slowly decomposed by boiling water with formation of carbon dioxide and ββ-diphenylpropionic acid. *Ethyl bromodiphenylmethylmalonate*, $CHPh_2\cdot CBr(CO_2Et)_2$, separates from alcohol in large, diamond-shaped plates, melts at 79—80°, and is readily soluble in acetone or ether and fairly so in alcohol. If this ester is left in contact with potassium hydroxide for several days, *potassium α-bromo-ββ-diphenylpropionate* is obtained, which is decomposed by boiling water with formation of carbon dioxide, potassium bromide, and stilbene. When the ester is boiled with alcoholic potassium hydroxide, it is converted into β-phenylcinnamic acid, which is also produced by the action of boiling alcoholic potassium hydroxide on ethyl bromodiphenylmethylmalonate. *α-Bromo-ββ-diphenylpropionic acid*, $CHPh_2\cdot CHBr\cdot CO_2H$, separates in crystals from a mixture of chloroform and light petroleum, is sparingly soluble in water, and slowly undergoes decomposition in aqueous solution into carbon dioxide, hydrogen bromide, and stilbene. *Ethyl O-acetyldiphenylmethylmalonate*, $CHPh_2\cdot C(CO_2Et):C(OAc)\cdot OEt$, obtained by the action of acetyl chloride on the ethereal solution of the magnesium derivative, crystallises from alcohol in large, lustrous plates, melts at 92°, is readily soluble in chloroform, acetone, or hot alcohol, and is hydrolysed by alcoholic potassium hydroxide with formation of potassium acetate and ethyl diphenylmethylmalonate. When this compound is boiled with an ethereal solution of magnesium phenyl bromide, ethyl diphenylmethylmalonate and diphenylmethylcarbinol are produced. In the preparation of this acetyl derivative, a small quantity of an

oily substance is formed, which appears to be a geometrical isomeride, and yields the same products with magnesium phenyl bromide.

By the action of bromodiphenylmethane on the magnesium compound obtained from ethyl benzylidenemalonate and magnesium phenyl bromide, an O-*diphenylmethyl* derivative of ethyl diphenylmethylmalonate, $CHPh_2\cdot C(CO_2Et):C(O\cdot CHPh_2)\cdot OEt$, is obtained, which crystallises in plates, melts at 132°, and is readily soluble in chloroform or acetone, and moderately so in alcohol or ether; when heated with hydrochloric acid in a sealed tube at 175—180° for eight hours, it is decomposed into carbon dioxide, ethyl chloride, and $\beta\beta$-diphenylpropionic acid.

Ethyl β-phenylethylmalonate, $CHPhMe\cdot CH(CO_2Et)_2$, prepared from ethyl benzylidenemalonate and magnesium methyl iodide, is a colourless liquid which boils at 230—235° under 15 mm. pressure. The corresponding *acid* crystallises in large plates, melts at 144°, is readily soluble in alcohol or ether, and moderately so in hot water, and when heated at 180° is decomposed into carbon dioxide and β-phenylbutyric acid. β-Phenylbutyric acid (Kohler and Reimer, this vol., i, 348) crystallises in large, lustrous prisms and melts at 47°.

a-Bromo-γ-phenylvaleric acid, $CHPhMe\cdot CH_2\cdot CHBr\cdot CO_2H$, obtained by the addition of bromine to the product of the action of magnesium ethyl bromide on ethyl benzylidenemalonate, crystallises from a mixture of chloroform and light petroleum, melts at 176°, decomposes above 190°, and is readily soluble in alcohol, ether, or chloroform, and very slightly so in water or light petroleum. When its *potassium* salt is heated by means of a current of steam, it undergoes decomposition with formation of phenylbutylene. E. G.

Behaviour of Hydroxysalicylic Acid [Quinolcarboxylic Acid] towards Oxidising Agents. VIKTOR JUCH (*Monatsh.*, 1905, **26**, 839—854. Compare Nef, Abstr., 1887, 255).—Quinolcarboxylic acid is obtained in a yield of 35 per cent. of the quinol, from which it is formed by Senhofer and Sarlay's method (Abstr., 1881, 1140), if xylene is used in the place of amyl alcohol. The *ethyl* ester forms almost colourless crystals and melts at 77°. On oxidation with ferric chloride in various solvents, the acid and its ester give blue to red colorations and amorphous substances which, from their odour and reaction with potassium iodide, appear to contain a small quantity of a quinone derivative.

The oxidation of quinolcarboxylic acid by manganese dioxide and concentrated sulphuric acid leads to the formation of a *product*, $C_{14}H_6O_6$, which crystallises from hot phenol or *o*-cresol as a yellow powder, melts above 360°, sublimes, with slight decomposition, in yellow, spicular prisms at 230° in a current of carbon dioxide, and when dry is stable in air. It is soluble in nitrobenzene, aniline, naphthalene, glacial acetic acid, or xylene, the solution in the last being violet by reflected and yellow by transmitted light. It dissolves in concentrated sulphuric acid to a green solution, and in aqueous alkali hydroxides or ammonia to solutions which become dark red owing to oxidation by the atmospheric oxygen. When distilled with zinc dust, it yields phenanthrene. The oxidation product

is a weak acid; the *potassium* salt, $C_{14}H_4O_6K_2$, crystallises in glistening, delicate needles which become orange-red when dried; the *sodium* salt crystallises from hot aqueous sodium carbonate in yellow needles. The *diacetyl* derivative, $C_{14}H_4O_6Ac_2$, crystallises in glistening, white leaflets or in needles, melts at 281—282°, commences to sublime at 200°, and is insoluble in water.

The constitution of the compound $C_{14}H_6O_6$ is discussed. G. Y.

An Oxidation Product of Homohydroxysalicylic Acid. W. Duregger (*Monatsh.*, 1905, **26**, 823—832. Compare Senhofer and Brunner, Abstr., 1881, 265; Brunner, Abstr., 1881, 1142).—Homohydroxysalicylic acid is oxidised by manganese dioxide and concentrated sulphuric acid to a *product*, $C_{16}H_{10}O_6$, which sublimes in long, yellow, prismatic needles, melts at about 360°, and is soluble in phenol, cresol, nitrobenzene, aniline, naphthalene, or aqueous alkali hydroxides. When distilled with zinc dust, the oxidation product yields a *hydrocarbon*, $C_{15}H_{14}$, which crystallises in white scales, melts at about 79°, and is oxidised by sodium dichromate in glacial acetic acid to a *substance* crystallising in microscopic, yellow needles and subliming at 320°. This dissolves in aqueous alkali hydroxides or carbonates, is reprecipitated by acids, and on distillation with calcium oxide yields a red liquid.

The oxidation product, $C_{16}H_{10}O_6$, is reduced by zinc dust in boiling aqueous potassium hydroxide solution to a *fluorenone* derivative, $C_{15}H_{12}O_5$, which crystallises from dilute alcohol in yellow needles, melts above 300°, dissolves in concentrated sulphuric acid to a yellow, slightly fluorescent solution, and forms a *tetra-acetyl* derivative, $C_{15}H_8O_5Ac_4$, crystallising in long, thin, white needles and melting above 300°. The fluorenone derivative is oxidised by ferric chloride or potassium dichromate in alcoholic or acetic acid solution to a *quinhydrone* derivative, $C_{15}H_{12}O_6$, which forms dark red crystals, melts at 220—230°, and dissolves in alcohol to a red solution, which is changed to yellow by the action of sulphur dioxide. G. Y.

Methyl Ethers of Quinolcarboxylic, Protocatechuic, and Gallic Acids. Carl Graebe and Ernst Martz (*Annalen*, 1905, **340**, 213—221).—Quinolcarboxylic acid is readily prepared by oxidising salicylic acid in alkaline solution with potassium persulphate. On treatment of the acid with methyl sulphate (2 mols.) in the presence of two equivalents of sodium hydroxide, the 5-methoxy-2-hydroxybenzoic acid, which is obtained by methylation with methyl iodide, is formed; it forms a very insoluble *calcium* salt; its *methyl* ester, which is formed to a small extent in the formation of the ether, is readily prepared by direct methylation, and is a liquid boiling at 235—240°; this ester is alone produced if the acid is treated with methyl sulphate and only one equivalent of sodium hydroxide. The dimethyl ether is formed if the methyl sulphate is in excess, but the methylation is not complete.

Methyl quinolcarboxylate is prepared by the hydrogen chloride method, and is a solid melting at 87·8°.

Protocatechuic acid readily yields the dimethyl ether when treated

with methyl sulphate in the presence of $3\frac{1}{2}$ mols. of sodium hydroxide. In the presence of less alkali hydroxide, *iso*vanillic, vanillic, and veratric acids are also produced.

Gallic acid yields a trimethyl ether readily, but on partial methylation only a monomethyl ether, the methoxyl group being in the para-position relative to the carboxyl group. Methyl gallate, on the other hand, yields the dimethyl ether, syringic acid, hydrolysis of the ester occurring in the process. Boiling of the trimethyl ether with 48 per cent. hydrobromic acid also gives this acid, which on heating yields pyrogallol 1 : 3-dimethyl ether, and on oxidation dimethoxyquinone.

K. J. P. O.

Methyleneoxyuvitic Acid. Chemische Fabrik auf Aktien vorm. E. Schering (D.R.-P. 158716).—Paraformaldehyde reacts with a solution of hydroxyuvitic acid in concentrated sulphuric acid at the ordinary temperature. The product, *methyleneoxyuvitic acid*, $CO_2H{\cdot}C_6H_2Me{<}\begin{matrix}O-CH_2\\ CO{\cdot}O\end{matrix}$, crystallises from dilute alcohol in thick, yellow needles, melts at 225°, and is insoluble in water or organic solvents, except alcohol and acetic acid.

C. H. D.

Transformation of Trimethylgallic Acid and Trimethylpyrogallolcarboxylic Acid into Derivatives of Pyrogallol Trimethyl Ether, Antiarol, and Hexamethoxydiphenyl. Carl Graebe and Moritz Suter (*Annalen*, 1905, **340**, 222—231).—Trimethylgallamide, $OMe{\cdot}C{<}\begin{matrix}C(OMe){\cdot}CH\\ C(OMe){:}CH\end{matrix}{>}C{\cdot}CO{\cdot}NH_2$, is prepared by converting trimethylgallic acid into the acid chloride by treatment with phosphorus pentachloride in benzene solution and then passing in ammonia. When acted on by an alkaline solution of sodium hypochlorite, *5-aminotrimethylpyrogallol*, $OMe{\cdot}C{<}\begin{matrix}C(OMe){\cdot}CH\\ C(OMe){:}CH\end{matrix}{>}C{\cdot}NH_2$, is obtained, melting at 113—114°; its *acetyl* derivative crystallises in needles melting at 124°. When the base is diazotised and the solution boiled, the 1 : 2 : 3-*trimethyl ether* of 1 : 2 : 3 : 5-*tetrahydroxybenzene* is obtained; it forms colourless crystals melting at 146°, and is identical with Kiliani's antiarol.

The *trimethyl ether* of *pyrogallolcarboxylamide*, prepared similarly to the gallamide, melts at 130—131°. From it *4-aminopyrogallol trimethyl ether*, $OMe{\cdot}C{<}\begin{matrix}C(OMe){\cdot}C(OMe)\\ CH=\!=\!=\!=C\end{matrix}{>}C{\cdot}NH_2$, is prepared; it is an oil, and yields a *hydrochloride* melting at 181°. *4-Chloropyrogallol trimethyl ether*, $C_9H_{11}O_3Cl$, is an oil and is prepared from 4-chloropyrogallol. *4-Iodopyrogallol trimethyl ether* forms brownish-yellow crystals melting at 40—41°. *5-Chloropyrogallol trimethyl ether*, prepared by diazotising the corresponding amino-derivative, forms crystals melting at 72°; the analogous 5-*iodo*-derivative crystallises in yellow plates melting at 82—83°.

3 : 4 : 5 : 3′ : 4′ : 5′-*Hexamethoxydiphenyl*, $C_6H_2(OMe)_3{\cdot}C_6H_2(OMe)_3$, is prepared by heating 5-iodopyrogallol trimethyl ether with copper at 270° and forms crystals melting at 126°; it can also be prepared from

hydrocedriret and methyl sulphate. 2 : 3 : 4 : 2′ : 3′ : 4′-*Hexamethoxydiphenyl* is prepared from the 4-iodo-derivative and melts at 123° ; it is also obtained from ellagic acid by melting with potassium hydroxide and treatment of the resulting product with methyl sulphate.

K. J. P. O.

Naphthoylbenzoic Acid. CARL GRAEBE (*Annalen*, 1905, **340**, 249—259).—1-Naphthoyl-2′-benzoic acid is best prepared by slowly adding aluminium chloride to a warm solution of naphthalene and phthalic anhydride in carbon disulphide. The *methyl* ester melts at 120°, and the *ethyl* ester at 123—124°. When the acid is warmed with phosphorus pentachloride in benzene solution, an *anhydride*,

$$\left[CO{<}{\overset{-O-}{\underset{C_6H_4}{}}}{>}C(C_{10}H_7)\right]_2O,$$

is produced, which forms crystals melting at 217°, and is only very slowly attacked by alkali hydroxides. The *acid amide*,

$$C_{10}H_7{\cdot}CO{\cdot}C_6H_4{\cdot}CO{\cdot}NH_2,$$

prepared by leading ammonia into a benzene solution of the acid containing phosphorus pentachloride, crystallises in colourless needles and melts at 215°.

When oxidised with an alkaline solution of permanganate, naphthoylbenzoic acid yields *diphthalylic acid*,

$$CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H,$$

which forms crystals melting at 270°. If naphthylbenzoic acid is heated with an excess of phosphorus pentachloride at 220°, naphthanthraquinone is formed quantitatively ; the quinone is also obtained by oxidation of naphthanthracene, and can be oxidised to diphthalylic acid.

K. J. P. O.

Tetrachloro- and Dichloro-naphthoylbenzoic Acids. CARL GRAEBE and WALTER PETER (*Annalen*, 1905, **340**, 259—266).—In order to prepare 1 : 2-naphthalenedicarboxylic acid, the chloronaphthoylbenzoic acids have been obtained, from which tetrachloronaphthanthraquinone might be prepared and thence the dibasic acid. The attempt was, however, unsuccessful.

3 : 4 : 5 : 6-*Tetrachloro-2-a-naphthoylbenzoic acid*,

$$C_{10}H_7{\cdot}CO{\cdot}C{<}\begin{matrix}C(CO_2H){\cdot}CCl\\CCl{=\!=\!=}CCl\end{matrix}{>}CCl,$$

prepared by the action of aluminium chloride on a solution of naphthalene and tetrachlorophthalic anhydride in carbon disulphide, forms yellow crystals melting at 229° ; the *sodium* salt crystallises with $4H_2O$. The *methyl* ester is readily prepared by direct esterification at the ordinary temperature and thus forms an exception to Victor Meyer's rule ; it forms crystals melting at 130°. When the acid is treated with concentrated sulphuric acid, tetrachloronaphthanthraquinone is not obtained, but a *sulphonic acid*, $C_{18}H_8O_5Cl_4S$, is formed. When heated with phosphorus pentachloride, tetrachloro-2-a-naphthoylbenzoic acid yields a *chloride*, $C_{18}H_7O_2Cl_5$, which forms crystals

melting at 214°. On oxidation with alkaline permanganate a *tetrachlorodiphthalylic acid*,

$$CH{<}{\substack{CH\text{———}CH\\ CH{:}C(CO_2H)}}{>}C{\cdot}CO{\cdot}CO{\cdot}C{<}{\substack{C(CO_2H){\cdot}CCl\\ CCl{=\!=}CCl}}{>}CCl,$$

is obtained as crystals melting at 290°.

3 : 6-*Dichloro-2-a-naphthoylbenzoic acid*, $C_{10}H_7{\cdot}CO{\cdot}C_6H_2Cl_2{\cdot}CO_2H$, prepared by adding aluminium chloride to a solution of naphthalene and 3 : 6-dichlorophthalic anhydride in carbon disulphide, melts at 207·5°, and is converted into α-naphthoic acid by fusing with sodium hydroxide at 290°; the *methyl* ester forms crystals melting at 144°. When the acid is oxidised by permanganate, 3 : 6-*dichlorodiphthalylic acid*, $CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}CO{\cdot}C_6H_2Cl_2{\cdot}CO_2H$, is formed, melting at 216°. Sulphuric acid converts the dichloro-α-naphthoylbenzoic acid into *dichloronaphthanthraquinonesulphonic acid*, $C_6H_2Cl_2{<}{\substack{CO\\ CO}}{>}C_{10}H_5{\cdot}SO_3H$.

K. J. P. O.

Compounds of β-Phenylhydroxylamine with Aromatic Aldehydes. GIUSEPPE PLANCHER and GALEAZZO PICCININI (*Atti R. Accad. Lincei*, 1905, [v], **14**, ii, 36—43).—β-Phenylhydroxylamine serves as a general reagent for aldehydes, with which it forms the corresponding phenylaldoximes of the formula $\substack{CHR\\ |\\ NPh}{>}O$. The following compounds have been prepared in this way.

Phenylbenzaldoxime, already obtained by Bamberger (Abstr., 1894, i, 412) and by Gattermann (Abstr., 1897, i, 189).

Phenylsalicylaldoxime, $\substack{OH{\cdot}C_6H_4{\cdot}CH\text{-}\\ \quad\quad\quad |\\ \quad\quad\quad NPh}{>}O$, separates from alcohol as a yellow, crystalline powder melting at 118°, and dissolves slightly in light petroleum and readily in benzene.

Phenylanisaldoxime, $\substack{OMe{\cdot}C_6H_4{\cdot}CH\text{-}\\ \quad\quad\quad |\\ \quad\quad\quad NPh}{>}O$, crystallises from alcohol in white needles melting at 118—119° and dissolves slightly in ether or light petroleum and readily in benzene.

Phenylhomosalicylaldoxime, $\substack{OH{\cdot}C_6H_3Me{\cdot}CH\text{-}\\ \quad\quad\quad |\\ \quad\quad\quad NPh}{>}O$, crystallises from alcohol in golden-yellow leaflets melting at 160°.

Phenylvanillaldoxime, already prepared electrolytically by the Farbenfabriken vorm. Friedr. Bayer (D.R.-P. 96564).

Phenylpiperonaldoxime, $CH_2{<}{\substack{O\\ O}}{>}C_6H_3{\cdot}CH{<}{\substack{O\\ |\\ NPh}}$, crystallises from alcohol or from a mixture of benzene and light petroleum in radiating masses of colourless needles melting at 135°.

Phenyl-m-nitrobenzaldoxime, $\substack{NO_2{\cdot}C_6H_4{\cdot}CH\text{-}\\ \quad\quad\quad |\\ \quad\quad\quad NPh}{>}O$, crystallises from alcohol in pale yellow, silky needles melting at 151°, and dissolves slightly in ether, light petroleum, or benzene.

Phenylcinnamaldoxime, $\mathrm{CHPh{:}CH{\cdot}\underset{NPh}{\underset{|}{C}H}}{>}O$, separates from alcohol in minute, yellow crystals melting at 150—151°.

Phenylcuminaldoxime, $\mathrm{CHMe_2{\cdot}C_6H_4{\cdot}\underset{NPh}{\underset{|}{C}H}}{>}O$, separates from alcohol in straw-yellow, prismatic crystals melting at 96—97°, and is soluble in benzene.

p-*Tolyl*-m-*nitrobenzaldoxime*, $\begin{matrix}\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH} \\ \mathrm{C_6H_4Me{\cdot}N}\end{matrix}{>}O$, crystallises from alcohol in shining scales melting at 161°, and is slightly soluble in light petroleum or ether, and more so in benzene.

It is noteworthy that such of the above compounds as contain a free hydroxyl group have a yellow colour. T. H. P.

Secondary Reaction of Magnesium Alkyl Haloids. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1905, **141**, 298—301. Compare Abstr., 1904, i, 666, 809).—When *cyclo*hexanone reacts with magnesium *iso*butyl bromide, not more that 10 per cent. of the theoretical yield of *tert.-iso*butyl*cyclo*hexanol is obtained. During this reaction, butylene is evolved, and the crystalline product $C_6H_{11}O{\cdot}MgI$ is formed, which in contact with water furnishes *cyclo*hexanol. Secondary reactions of this type occur as a rule only to a slight extent when the Grignard reaction is applied to aliphatic or aromatic aldehydes, chloral being the most notable exception. With ketones, and especially cyclic ketones, on the contrary, the secondary reaction assumes greater importance. The nature of the alkyl group in the magnesium alkyl haloid used also exerts some influence on the extent to which the secondary reaction takes place; thus *iso*butyl favours its occurrence, whilst primary aliphatic alkyl groups as a rule show this tendency to a much less extent, and aromatic alkyl groups do not exhibit it at all. Magnesium haloid derivatives of *sec.*-alkyl groups always furnish the secondary reaction to a greater or less extent. A number of cases illustrating these observations are quoted.

T. A. H.

ψ-Nitrosites of Unsaturated Ketones. HEINRICH WIELAND and SIEGFRIED BLOCH (*Annalen*, 1905, **340**, 63—85. Compare Abstr., 1904, i, 54, 415, 596).—The addition of N_2O_4 to the ethylene linking of phenylethylenes, CHPh:CHR, takes place in two ways according as the group R is of positive or of negative character: if R is positive, bimolecular ψ-nitrosites are formed, but if R is negative, as in unsaturated ketones or aldehydes, saturated unimolecular compounds are produced. The presence of positive substituents in the benzene nucleus neutralises the effect of the negative character of R; thus, for example, whilst benzylideneacetone or benzylideneacetophenone do not give nitrosites, the corresponding anisylidene compound yields such a derivative.

The ψ-nitrosites break up, when boiled with alcohol, into the unimolecular nitro-oximes, $\cdot C(NOH){\cdot}CH(NO_2){\cdot}$, which then lose water,

forming glyoximeperoxides, $\begin{matrix}\cdot C & \text{——} & C\cdot \\ \| & & \| \\ N\cdot O & \cdot & O\cdot N\end{matrix}$, if positive groups are present in the benzene nucleus. The nitro-oximes can also lose water in another manner from the corresponding enol, $\cdot C(NOH)\cdot C(NO_2)\colon C(OH)\cdot$, yielding β-nitro*iso*oxazoles, $\cdot C\lessdot\begin{matrix}C(NO_2)\\ N\text{——}O\end{matrix}\gtrdot C\cdot$. The anisylideneacetone ψ-nitrosites yield nitro-oximes which lose water, forming pyrrole derivatives, the methyl group sharing in the condensation, thus: $OMe\cdot C_6H_4\cdot C(NOH)\cdot CH(NO_2)\cdot CO\cdot CH_3 \longrightarrow$

$$OMe\cdot C_6H_4\cdot \begin{matrix}C\colon C(NO_2)\\ |\quad\quad \\ NH\text{—}CH_2\end{matrix}\!\!>\!CO.$$

Anisylideneacetophenone ψ-nitrosite,

$$N_2O_2[CH(C_6H_4\cdot OMe)\cdot CHBz\cdot NO_2]_2,$$

prepared by passing nitrous fumes into an alcoholic solution of anisylideneacetophenone in absolute alcohol cooled to 0°, crystallises in yellow needles melting and decomposing at 112°, and gives with sulphuric acid an intense red coloration. Boiling with alcohol converts it into 4-*nitro*-5-*phenyl*-3-*anisyl*iso*oxazole*,

$$OMe\cdot C_6H_4\cdot C\lessdot\begin{matrix}C(NO_2)\\ N\text{——}O\end{matrix}\gtrdot CPh,$$

which crystallises in needles and dissolves in alcoholic potassium hydroxide. When reduced with zinc dust and acetic acid in the presence of methyl alcohol, 4-*amino*-5-*phenyl*-3-*anisyl*iso*oxazole*, $C_{16}H_{14}O_2N_2$, is obtained as crystals melting at 123°; its *hydrochloride* melts at 185°. The *nitronitrite*, $OMe\cdot C_6H_4\cdot CH(O\cdot NO)\cdot CH(NO_2)\cdot COPh$, is formed at the same time as the ψ-nitrosite, and is obtained by evaporating the ethereal mother-liquor; it is decomposed by ammonia into anisaldehyde and nitroacetophenone, and when shaken with dilute sodium hydroxide into *anisylidene-α-nitroacetophenone*, $OMe\cdot C_6H_4\cdot CH\colon C(NO_2)\cdot COPh$, a viscid, yellow oil which decomposes explosively when heated in a vacuum at 115°.

Anisylideneacetone ψ-nitrosite, $C_{22}H_{24}O_{10}N_4$, is a white, crystalline powder decomposing at 111°, and when boiled with alcohol is converted into 4-*nitro*-5-*anisyl*-3-*pyrrolone*; the latter crystallises in golden-yellow needles melting at 89°, and gives an olive-green coloration with sulphuric acid. On reduction with stannous chloride and hydrochloric acid, 4-*amino*-5-*anisyl*-3-*pyrrolone hydrochloride*, $C_{11}H_{13}O_2N_2Cl$, is obtained in needles melting at 214°; the *base* forms crystals melting at 97°. α-*Nitroanisylideneacetone*, $OMe\cdot C_6H_4\cdot CH\colon CAc\cdot NO_2$, is obtained by allowing the ethereal mother-liquor, from which the ψ-nitrosite has separated, to remain in contact with water; it crystallises in four-sided prisms melting at 124°, and with sulphuric acid gives an orange coloration which passes into violet; dilute sodium hydroxide converts it into β-nitro-α-anisylethylene (m. p. 87°), and alcoholic ammonia gives rise to nitroacetone. K. J. P. O.

Condensation of Naphthalaldehydic Acid with *m*-Tolyl Methyl Ketone, Pinacoline, and Acenaphthenone. Siegfried Wiechowski (*Monatsh.*, 1905, **26**, 749—763. Compare Zink, Abstr., 1902, i, 34, 159; Goldschmiedt and Krezmař, Abstr., 1902, i, 41;

Luksch, this vol., i, 68).—m-*Tolyl naphthalidomethyl ketone*, formed by warming naphthalaldehydic acid with *m*-tolyl methyl ketone in dilute sodium hydroxide solution at 38° for 48—72 hours, is precipitated on addition of hydrochloric acid to the reaction mixture in large, yellow, oily drops which change into the colourless, crystalline *pseudo*-acid, $CO<\genfrac{}{}{0pt}{}{C_{10}H_6}{O}>CH\cdot CH_2\cdot CO\cdot C_7H_7$. This melts at 118—120°, is easily soluble in hot alcohol, hot glacial acetic acid, benzene, or chloroform, but only slightly so in ether, and dissolves in aqueous potassium hydroxide or sodium carbonate to form yellow solutions which decompose on boiling, giving an odour of *m*-tolyl methyl ketone.

The *oxime*, $CO<\genfrac{}{}{0pt}{}{C_{10}H_6}{O}>CH\cdot CH_2\cdot C(C_7H_7)\colon N\cdot OH$, formed by the action of hydroxylamine hydrochloride on the *pseudo*-acid in alcoholic solution, crystallises in colourless, probably monoclinic crystals, melts at 163°, has a neutral reaction to litmus, is insoluble in cold, but is decomposed by warm, aqueous alkali hydroxides, and is decomposed into hydroxylamine and the *pseudo*-acid when boiled with hydrochloric acid. The action of hydroxylamine and aqueous sodium hydroxide on naphthalidomethyl *m*-tolyl ketone in alcoholic solution leads to the formation of two products: (*a*) a small quantity of a *substance* which crystallises from glacial acetic acid, melts and decomposes at 235°, and contains nitrogen, and (*b*) a yellow, crystalline, *sodium* salt of the oxime or of the oxamino-oxime anhydride of *m*-tolyl naphthalidomethyl ketone.

The phenylhydrazone, $C_{27}H_{22}O_2N_2$, separates from glacial acetic acid in small, yellow crystals, melts at 152—155°, is insoluble in aqueous alkali hydroxides, is decomposed with formation of phenylhydrazine by concentrated or by hot alcoholic hydrochloric acid, and dissolves in concentrated sulphuric acid to a red solution which darkens on addition of potassium dichromate.

m-*Tolacylnaphthalimidine*, $CO<\genfrac{}{}{0pt}{}{C_{10}H_6}{NH}>CH\cdot CH_2\cdot CO\cdot C_7H_7$, formed by shaking *m*-tolyl naphthalidomethyl ketone with saturated aqueous ammonia, forms slender, white needles, melts at 152—154°, and when heated with hydrochloric acid, or more rapidly but with partial decomposition when heated with aqueous potassium hydroxide, is converted into a yellow *isomeride* which melts and partially decomposes at 234°, and is decomposed by boiling aqueous potassium hydroxide or hydrochloric acid.

Naphthalidopinacolin, $CO<\genfrac{}{}{0pt}{}{C_{10}H_6}{O}>CH\cdot CH_2\cdot CO\cdot CMe_3$, formed by the condensation of naphthalaldehydic acid with pinacolin in dilute sodium hydroxide solution, separates from alcohol in heavy crystals, melts at 113—114°, and is decomposed by boiling aqueous alkali hydroxides. The *oxime*, $CO<\genfrac{}{}{0pt}{}{C_{10}H_6}{O}>CH\cdot CH_2\cdot C(NOH)\cdot CMe_3$, formed by the action of hydroxylamine hydrochloride on naphthalidopinacolin in alcoholic solution, melts at 187—189° and is insoluble in aqueous alkali hydroxides. No imidine could be obtained by treating naphthalidopinacolin with ammonia.

The *condensation product* of naphthalaldehydic acid with acenaphthenone, $\begin{array}{l}C_{10}H_6\cdot CH\cdot CH \\ | \quad\quad\quad | \quad\quad | \\ CO\text{---}O \quad CO\end{array}>C_{10}H_6$, forms transparent crystals, melts at 226—227°, and remains unchanged when shaken with saturated aqueous ammonia. G. Y.

[Methoxy-derivatives of Anthraquinone.] Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 158257).—A solution of bromine in glacial acetic acid converts alizarin 2-methyl ether into 4-*bromoalizarin 2-methyl ether*, which crystallises from acetic acid in orange needles, melts at 234—235°, and dissolves sparingly in alcohol, more readily in benzene. It is insoluble in sodium carbonate, but dissolves in sodium hydroxide to a red solution, which deposits the *sodium* salt on cooling.

When boiled with *p*-toluidine, 4-p-*toluidinoalizarin 2-methyl ether*, $C_6H_4<^{CO}_{CO}>C_6H(OMe)(OH)\cdot NH\cdot C_6H_4Me$, is formed, and crystallises in glistening, violet needles, soluble in alcohol to a reddish-violet solution, and in concentrated sulphuric acid to a blue solution. A similar *compound* is obtained from aniline. On sulphonating at the ordinary temperature with fuming sulphuric acid, red or violet dyes are obtained, yielding green shades with chromium salts. C. H. D.

Preparation of Camphor. Chemische Fabrik auf Aktien vorm. E. Schering (D.R.-P. 158717).—Whilst bornyl acetate only yields 10 per cent. of camphor on oxidation (Schrötter, Abstr., 1882, 66), *iso*bornyl acetate yields as much as 90 per cent. of camphor on oxidation with chromic acid, nitric acid, potassium permanganate, or Caro's acid. The *iso*bornyl acetate obtained in the preparation of *iso*borneol from camphene may be employed without saponification. Less favourable results are obtained with the formate or benzoate.

C. H. D.

Terpenes and Ethereal Oils. Otto Wallach (*Annalen*, 1905, **340**, 1—16. Compare Abstr., 1903, i, 103, 105, 576; 1904, i, 1035).—The nitrite of β-phellandrene is best prepared by the action of nitrous acid on a solution of phellandrene in light petroleum; the small yield (25 per cent.) is due to the fact that part of the hydrocarbon escapes the action of the nitrous acid and that part of the nitrite is oxidised to nitrophellandrene and other compounds. Pure phellandrene nitrite is completely, although slowly, soluble in 10 per cent. sodium hydroxide.

On reducing nitrophellandrene in acetic acid by zinc dust or in alcohol by sodium, compounds are obtained which are partly of basic character and partly substances containing oxygen; they belong to the hydroaromatic group. *Dihydrocuminaldehyde*, $C_{10}H_{14}O$, was obtained by reduction with zinc dust and acetic acid after removal of the basic products; it is an oil boiling at 111—112° under 13 mm. pressure; its *semicarbazone* crystallises in needles melting at 200—202°. When oxidised by sodium hypobromite, cumic acid is formed, whilst silver oxide gives as well *dihydrocumic acid*, $C_{10}H_{14}O_2$, which melts above 130°. With sodium and alcohol as the reducing agent, cuminaldehyde,

and not dihydrocuminaldehyde, is produced together with other substances; it was recognised in the form of its aldoxime (m. p. 58—59°)

The basic products of reduction, which are easily separated as hydrochlorides, consist of a mixture of hydrocuminylamine (di- or tetra-hydrocuminylamine) with cuminylamine. The *hydrocuminylamine* is identical with Pesci's aminophellandrene, and is readily isolated as its *carbamide,* which is but sparingly soluble and crystallises in broad lamellæ melting at 160—161°, and has $[\alpha]_D$ $+58.566°$ in alcoholic solution.

These results show that β-phellandrene has a methylene group as a side-chain with an *iso*propyl group in the para-position; further, from the molecular refraction it follows that two ethylene linkings are present, and from the optical activity an asymmetric carbon atom. The formula $CH_2{:}C{<}\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH{=}CH}{>}CHPr^\beta$ expresses these facts; the nitrite then has the formula $NO_2\cdot CH_2\cdot C(NO){<}\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH{=}CH}{>}CHPr^\beta$, and the β-phellandrenediamine, obtained by careful reduction of the nitrite in acid solution, the formula

$$NH_2\cdot CH_2\cdot C(NH_2){<}\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH{=}CH}{>}CHPr^\beta;$$

either the formula $NO_2\cdot CH_2\cdot C{\lessdot}\genfrac{}{}{0pt}{}{CH\cdot CH_2}{CH{=}CH}{>}CHPr^\beta$ or the formula $NO_2\cdot CH{:}C{<}\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH{=}CH}{>}CHPr^\beta$ must then be ascribed to nitrophellandrene.

*iso*Butyric acid is the final product when phellandrene is oxidised with excess of permanganate. When the hydrocarbon is kept in large excess and the temperature low, a *glycol,*

$$OH\cdot CH_2\cdot C(OH){<}\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH{=}CH}{>}CHPr^\beta,$$

is formed together with a considerable quantity of volatile and non-volatile acids; the glycol is a colourless liquid boiling at 150° under 10 mm. pressure, and when treated with dilute sulphuric acid is converted into a *tetrahydrocuminaldehyde,* $CHPr^\beta{<}\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH{=}CH}{>}CH\cdot CHO$, which is a liquid boiling between 220° and 230°, and having a sp. gr. 0·93 at 20° and n_D 1·4903 at 20°. The *semicarbazone* crystallises in needles melting at 204—205°, and the *oxime* in six-sided plates melting at 87°. When oxidised with silver oxide, the aldehyde yields *tetrahydrocumic acid,* $C_{10}H_{16}O_2$, which melts at 143—144°. K. J. P. O.

Camphene. STEFAN MOYCHO and FRANZ ZIENKOWSKI (*Annalen,* 1905, **340**, 17—63. Compare Abstr., 1904, i, 438).—Since the evidence for Wagner's formula for camphene,

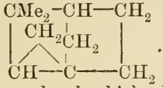
$$\begin{array}{lcl} & CMe_2\cdot CH\cdot CH_2 & \\ | & CH_2 & | \\ CH_2{:}C & \text{——} & CH\cdot CH_2 \end{array}$$

is indirect, an attempt has been made to obtain more certain proof.

From the oxidation products of camphene (*loc. cit.*), two additional acids have been isolated, the sodium salts of which are but sparingly

soluble. One acid, $C_{10}H_{14}O_3$, melts at 139·5° and the other, which has not been investigated fully, at 90°. On dry distillation of a liquid mixture of these acids, a lactone, $C_9H_{14}O_2$, is obtained crystallising in monoclinic plates and melting at 95—96°.

The cyclene (*loc. cit.*), which is converted into bornyl acetate by warming with acetic acid and sulphuric acid, is best represented by the formula



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Camphene glycol, which when pure melts at 200°, yields on esterification with benzoyl chloride in pyridine solution a *monobenzoate*, $C_{10}H_{17}O_2Bz$, which crystallises in prisms melting at 88°, and is reconverted into the glycol on hydrolysis. On treatment with phosphorus pentachloride or hydrogen chloride in chloroform solution, the monobenzoate is converted into an unsaturated *monobenzoate*, $C_{10}H_{15}OBz$, which melts at 85—86°, and on hydrolysis with alcoholic potassium hydroxide yields camphenilanaldehyde, and on oxidation with potassium permanganate camphenilone. These facts are in favour of Wagner's formula for camphene in that the group $\mathord{:}C\mathord{:}CH_2$ is present, whilst they are opposed to Bredt's view of the changes of camphene. The transformations from camphene through the glycol to the aldehyde are represented thus: $C_8H_{14}\mathord{:}C\mathord{:}CH_2 \longrightarrow C_8H_{14}\mathord{:}C(OH)\cdot CH_2\cdot OH \longrightarrow C_8H_{14}\mathord{:}C(OH)\cdot CH_2\cdot OBz \longrightarrow C_8H_{14}\mathord{:}C\mathord{:}CH\cdot OBz \longrightarrow C_8H_{14}\mathord{:}C\mathord{:}CH\cdot OH \longrightarrow C_8H_{14}\mathord{:}CH\cdot CHO$. All these observations are in favour of the view that the hydration product of camphene is a true glycol.

When the pure glycol is oxidised by permanganate in 4 per cent. aqueous solution, besides camphenilone and camphenilic acid, a new *acid*, $C_{10}H_{14}O_3$, is obtained crystallising in prisms melting at 139°. The relation of this acid to camphenilic acid has not yet been demonstrated; it is possible that the erroneous statement that camphenecamphoric acid is obtained in the oxidation of camphene is due to the new acid being mistaken for camphenecamphoric acid; the melting points lie near together.

A consideration of numerous observations, recorded both in this paper and previously, lead to the conclusion that the camphene obtained from *iso*borneol consists of a mixture of three hydrocarbons: (i) camphene, the oxidation products of which are camphene glycol, and then camphenilic acid and camphenilone; (ii) camphene from which camphenecamphoric acid can be obtained, and (iii) the saturated cyclene, of which the oxidation products have not yet been investigated. The first of these three hydrocarbons alone contains the group $\mathord{:}C\mathord{:}CH_2$.

The neutral oxidation product of camphene, $C_{10}H_{16}O_2$ (*loc. cit.*), which melts at 169—170°, with benzoyl chloride in pyridine solution yields a *monobenzoate* melting at 71°, which, however, is not attacked by phosphorus pentachloride; the substance only contains one hydroxyl group, and must, therefore, be a hydroxyoxide. It is not probable that the hydroxyoxide is formed from camphene glycol, since neither the oxide nor its oxidation product, the acid $C_{10}H_{14}O_3$, melting at 198—200°, can be found among the oxidation products of the glycol.

It is worthy of note that the acid $C_{10}H_{14}O_3$ (m. p. 138·5°), obtained from the glycol, can be changed into the isomeric acid from the hydroxyoxide. It is suggested that the hydroxyoxide is formed from cyclene.

The acid $C_{10}H_{14}O_3$ (m. p. 138·5°), which is formed, together with camphenilic acid and an acid melting at about 90°, in the oxidation of camphene, is isolated in the form of a sparingly soluble *sodium* salt, and crystallises in large, four-sided prisms. The acid reacts with one mol. of phosphorus pentachloride, and not at all with semicarbazide; one atom of oxygen must, therefore, be present as oxide. It forms an additive product with hydrogen chloride, $C_{10}H_{15}O_3Cl$, which contains a hydroxyl group and reacts with benzoyl chloride in the presence of pyridine, yielding a *benzoate* melting at 110°. The additive product is reconverted into the original acid by treatment with alcoholic potassium hydroxide, but if first heated with silver acetate and then hydrolysed, an isomeric acid (m. p. 198—200°) is obtained which is identical with the product of oxidation of the hydroxyoxide mentioned in the foregoing paragraph.

Camphenecamphoric acid, $\begin{array}{l} CMe_2\text{—}CH\cdot CO_2H \\ |\qquad\quad\ \ CH_2 \\ CHMe\cdot CH\cdot CO_2H \end{array}$ (?), is the main oxidation product of the camphene obtained from *iso*borneol, and is formed from the neutral oxidation product remaining after campheneglycol and the hydroxyoxide have been removed. This neutral substance on keeping gradually changes into the acid. The acid yields a *diamide*, $C_{10}H_{18}O_2N_2$, crystallising in scales melting at 222°, from which the *carbamate*, $C_8H_{14}(NH\cdot CO_2Me)_2$, crystallising in plates melting at 114°, can be prepared by the action of bromine and sodium methoxide. The *dianilide* crystallises in needles melting at 210°. The *dinitrile*, prepared by dry distillation of the diamide, is a liquid boiling at 173—175° under 14 mm. pressure, and when reduced with sodium and alcohol yields *camphenecamphoryldiamine*, $C_8H_{14}(CH_2\cdot NH_2)_2$.

Camphenilic acid can be acylated when the ester is treated with acyl chlorides in the presence of pyridine. The *acetyl* derivative is a liquid boiling at 138·5—139·5° under 12 mm. pressure, and the *benzoyl* derivative a solid melting at 168°. When heated above its melting point, the acid decomposes into carbon dioxide, water, and a hydrocarbon, C_9H_{14}, which boils at 137·5—138·5° and is possibly identical with Jagelki's camphenylene.

When camphenilone is treated with sodium and amyl formate in order to prepare a hydroxymethylene derivative, the *pinacone*, $C_{18}H_{30}O_2$, is formed, two modifications melting at 173—173·5° and at 172·5—173° respectively being obtained; camphenilone does not contain a carbonyl group attached to a methylene group. The ketone cannot be readily oxidised, but is converted by phosphorus pentachloride into a *dichloride*, $C_9H_{14}Cl_2$, which forms soft crystals melting at 174°. Treatment with sodium decomposes this chloride, apobornylene (m. p. 34°, and b. p. 136—137°) and other substances being produced.

The alcohol, methylcamphenilol, prepared from camphenilone (*loc.*

cit.), is a structural isomeride of *iso*borneol, since the two alcohols behave differently on oxidation with chromic acid. K. J. P. O.

Essential Oils from Liverworts. KARL MÜLLER (*Zeit. physiol. Chem.*, 1905, **45**, 299—319).—All liverworts appear to contain essential oils. From *Mastigobryum trilobatum*, an oil distilling at 260—265° was obtained. It has the composition $C_{10}H_{16}$, sp. gr. 0·946 at 20°, and $[\alpha]_D + 25·95°$, and on oxidation yields a ketone, $C_{10}H_{16}O$. A fraction boiling at 270—285° with $[\alpha]_D + 42·21°$ and sp. gr. 0·820 was also obtained. *Leioscyphus Taylori* yields a considerable amount of a green oil with a high sp. gr. and large saponification value, and probably contains two alcohols, $C_{15}H_{26}O$, and a terpene or sesquiterpene. *Madotheca levigata* yields an oil of low sp. gr. and rich in readily volatile compounds. The fraction boiling at 280° is characterised by its high rotation (+132°) and seems to contain about 10 per cent. of an alcohol, $C_{10}H_{18}O$. *Alicularia scalaris* yields a small amount of a lævorotatory yellow oil. J. J. S.

Balata. ALEXANDER TSCHIRCH and E. SCHERESCHEWSKI (*Arch. Pharm.*, 1905, **243**, 358—377).—Balata, or "Surinam gutta-percha," the most important substitute for gutta-percha, is the product of *Mimusops globosa* (or *M. Balata*), one of the *Sapotaceæ*, which grows in Guiana. Of the sample examined, water dissolved 5·7, alcohol 41·5 (resin), acetone 42·5, ether 87, and chloroform 87 (resin + gutta) per cent. The loss at 100° in several hours (moisture) was 1·72, ash 0·96, and impurities 10·5 per cent.

No substances volatile with steam were present. Water extracted a *gum* insoluble in alcohol, mixed with *proteid* material, from which it was freed by means of tannic acid; it amounted then to 1·5 per cent. of the drug. The gum was optically inactive, even after boiling with acid, and was not fermented by yeast; it reduced Fehling's solution and gave the α-naphthol-sulphuric acid reaction; when it was charred or boiled with dilute sulphuric acid, the vapours evolved gave the reaction for furfuraldehyde, and when it was fused with potassium hydroxide the vapour gave the reaction of pyrrole; it gave 6·5 per cent. ash. No oxydase was present.

The material was then extracted with boiling alcohol, which dissolved the *resin*. As the solution cooled a substance separated, which was further separated by treatment with alcohol at 50° into the readily soluble *β-balalban*, $C_{27}H_{44}O_2$ or $C_{27}H_{46}O_2$ (molecular weight determined), which crystallises in lustrous scales and melts at 108—109°, and the sparingly soluble *α-balalban*, $C_{27}H_{42}O_2$, which crystallises in needles and melts at 230—231°. The former was obtained in much larger amount; when boiled with alcoholic potassium hydroxide, it yielded a small quantity of a *substance* which melted at 116—117° and contained C 82·9, H 12·3 per cent. No cinnamic ester is present in the drug; neither is it, however, in all samples of gutta-percha. When the alcoholic liquid from which the alban had separated was poured into very dilute hydrochloric acid, *balafluavil*, $C_{10}H_{18}O$, was precipitated in amount equal to about 1·5 per cent. of the drug; it is a sticky, amorphous substance.

The residual material was next dissolved in chloroform, the solution diluted with half its volume of ether, and alcohol added until a permanent turbidity resulted; *balagutta*, $C_{10}H_{18}$, separated gradually in needles curved like sickles or commas; it is very unstable in the presence of air, although the drug which contains it is stable. By adding much alcohol to the mother liquor, *balalbanan* was precipitated; it was crystallised from a mixture of alcohol and ether, when it melted at 55—56° and contained C 77·7—82·3, H 11·9—12·2 per cent.; it oxidises very readily in the air. C. F. B.

Gentiin. GEORGES TANRET (*Compt. rend.*, 1905, **141**, 263—264).—*Gentiin*, $C_{25}H_{28}O_{14}$, occurs in the mother liquors resulting from the purification of gentiopicrin (this vol., i, 655). It separates from boiling alcohol in microscopic, slightly yellow needles, melts and decomposes at 274°, and gives a green coloration with nitric acid and greenish-black with ferric chloride. Gentiin is slowly hydrolysed by dilute sulphuric acid at 100°, forming dextrose (1 mol.), xylose (1 mol.), and *gentienin*, $C_{14}H_{10}O_5$ (1 mol.). The last-mentioned substance crystallises from boiling alcohol in sulphur-yellow needles, begins to sublime at 195°, and melts at 225°. It is isomeric with gentisin, but melts at a lower temperature and gives a yellow in place of a green coloration with nitric acid. It is stated that gentiin is the first recorded glucoside yielding xylose as a product of hydrolysis. T. A. H.

Process of Dyeing Animal Textile Fibres. P. GELMO and WILHELM SUIDA (*Monatsh.*, 1905, **26**, 855—878. Compare Suida, this vol., i, 457; Knecht, Abstr., 1889, 49).—The affinity of wool which has been treated with very dilute aqueous or alcoholic sulphuric acid and washed with hot water is diminished towards basic but increased towards acid dyes, but the affinity towards acid dyes is diminished if the treatment and washing are carried out at the laboratory temperature. The action of hydrochloric acid on wool is similar to that of sulphuric acid; the behaviour towards dyes of wool which has been treated with dilute acetic acid and thoroughly washed is the same as that of untreated wool, but the affinity towards basic dyes is diminished if the dyeing takes place immediately after the treatment with acetic acid and without washing. The effect of tartaric acid on wool is intermediate between that of sulphuric acid and that of acetic acid.

When boiled with water or an aqueous solution of aluminium sulphate or of sulphuric acid, wool undergoes such a considerable loss in weight, owing to the formation of soluble amino-acids, that quantitative mordanting experiments cannot be carried out. Wool and silk were boiled with $N/10$ ammonia, hydrochloric acid, and sulphuric acid, and the reagent remaining unabsorbed titrated, using methyl-orange as indicator; the reaction was complete in five minutes. Two specimens of wool and one of silk were found to absorb ammonia, hydrochloric acid, and sulphuric acid in the respective proportions: $NH_3 : 2HCl : 2{\cdot}4H_2SO_4/2$; $NH_3 : 2HCl : 2{\cdot}1H_2SO_4/2$; and $6{\cdot}4NH_3 : HCl : 2H_2SO_4/2$ (compare Mills and Takamine, Trans., 1883, **43**, 142). The difference in behaviour of the two specimens of wool agrees with the fact that some wools are alkaline,

whilst others are neutral to phenolphthalein. The dyeing of purified wool by pure acid dyes set free from their salts by means of fuming hydrochloric acid, washed and dried, is not increased by the addition of mineral acids. Owing to its acid nature, wool forms salts when treated with aqueous alkali carbonates or with hard water, and it is to neutralise these that the mineral acid necessary in dyeing is required. When heated with alcoholic potassium hydroxide and washed with water, wool forms potassium compounds which give stronger colours with benzopurpurin 6B and with Bordeaux extra. This behaviour is not altered by steeping the treated wool in very dilute acetic acid.

Wool which has been heated on the water-bath with 0·1 per cent. alcoholic zinc chloride gives weaker colours with basic dyes, but a stronger colour with azomagenta G in a neutral bath, than when heated with aqueous zinc chloride. No difference could be observed in the behaviour towards alizarin-red S or anthracene-blue WG of wool mordanted with chromium sulphate with or without previous treatment with dilute sulphuric acid; but wool mordanted with aluminium sulphate after treatment gives stronger colours, whilst wool mordanted with ferric sulphate after treatment gives weaker colours, than does wool mordanted with these salts without previous treatment with sulphuric acid. Untreated wools mordanted with chromium, aluminium, or ferric sulphates behave towards basic and acid dyes in the same manner as does wool treated with sulphuric acid but not mordanted. This behaviour is reversed by treatment of the mordanted wool with aqueous ammonium carbonate. Wool which has been boiled with $N/10$ aluminium acetate or tartrate cannot be dyed with direct dyes, which points to neutralisation of the acid groups of the wool.

Wool is hydrolysed by boiling water, or more quickly by dilute mineral acids or solutions of mordanting salts; its soluble products of hydrolysis are therefore always formed during the process of dyeing. The reactions of these soluble products show the presence of a peptone, which, on further hydrolysis, must break down to simpler amino-acids. The aminobenzoic acids precipitate crystal-violet O and pararosaniline from neutral baths, as also azomagenta G from its solution in weak acetic acid, and assist therefore the process of dyeing, whilst the fatty amino-acids do not do so. The presence of peptone causes colours obtained on dyeing wool with basic dyes in neutral solutions not to be fast to soaping, whilst dyeing is not obtained with acid dyes in neutral solution, but in a weak acid bath acid dyes give fast colours.

Experiments show that whilst untreated wool is only moderately dyed, wool which has been heated with 0·5 per cent. aqueous or alcoholic sulphuric acid is intensely dyed by azomagenta G or crystal-ponceau, but only the dyed wool previously treated with alcoholic sulphuric acid is fast to soaping.

The hydrolysis of wool is necessary to the process of dyeing. It is possible that wool is an anhydro-compound, the active groups of which are formed only on hydrolysis. When treated with alcoholic sulphuric acid, wool apparently loses its acid characters, becoming basic and capable of uniting with mineral acids. The salts so formed undergo double decomposition with acid dyes, but cannot enter into reaction with basic dyes. G. Y.

Homologues of Quinophthalone. ALEXANDER EIBNER (D.R.-P. 158761. Compare Abstr., 1904, i, 930, 931).—The mixture of quinophthalones and *iso*quinophthalones, obtained by the action of phthalic anhydride on quinaldine derivatives, may be converted into pure quinophthalones by warming on the water-bath with an alcoholic solution of sodium ethoxide. The sodium derivatives thus obtained are decomposed by boiling water and dried at 100°.

6:8-*Dimethylquinophthalone*, $C_9NH_4Me_2\cdot CH\colon C_8H_4O_2$, forms a golden-yellow powder and melts at 290°. 5:6:8-*Trimethylquinophthalone* forms a dark golden-yellow powder and melts at 294°. β-*Naphthaquinophthalone*, $C_{13}NH_8\cdot CH\colon C_8H_4O_2$, forms an orange powder and melts at 326°.

The dyeing power, fastness towards light, and insolubility in alcohol or chloroform increase with increase in the molecular weight.

C. H. D.

Quinine Formates. HUNKIARBÉYENDIAN LACROIX (*J. Pharm. Chim.*, 1905, [vi], 22, 99—103).—Normal quinine formate,

$$C_{20}H_{24}O_2N_2,2H_2CO_2,$$

obtained by dissolving one part of quinine in two parts of formic acid, is an unstable salt which dissolves in water giving an acid solution; it crystallises in long, white, glistening needles which melt at 95° and lose formic acid below 50°. Basic quinine formate, $C_{20}H_{24}O_2N_2,H_2CO_2$, is prepared by adding the calculated amount of glacial formic acid to quinine suspended in water at 50°; it crystallises from the solution on cooling in tufts of white, silken needles melting at 132°; it contains more quinine than any other quinine salt; its aqueous solution, which is neutral to litmus and is not fluorescent, has $[\alpha]_D -141{\cdot}1°$ at 21°. A 2 per cent. solution at 21° has n_D 1·336. It dissolves in nineteen parts of water at 16° and in six parts at 42°. P. H.

Sparteine. CHARLES MOUREU and AMAND VALEUR (*Compt. rend.*, 1905, 141, 261—262 and 328—330. Compare this vol., i, 608—609, and Willstätter and Marx, *ibid.*, i, 544).—The products described in the first of these papers were obtained in the course of an investigation of the substances produced by the exhaustive methylation of sparteine. The alkylsparteines described are in each case mixtures of isomerides and are tertiary unsaturated bases, which readily reduce permanganate.

Methylsparteine, $N\colon C_{15}H_{25}NMe$, obtained by distilling methylsparteinium hydroxide, $N\colon C_{15}H_{26}NMe\cdot OH$ (sparteinemethylammonium hydroxide), prepared from sparteine α-methiodide by the action of silver hydroxide, may be separated into fractions boiling between 171° and 175° under 11·5 mm. pressure and having $[\alpha]_D$ ranging from $-19{\cdot}67°$ to $-40{\cdot}0°$ in alcohol. *Dimethylsparteine*, similarly prepared from sparteine dimethylammonium hydroxide, is an oil boiling at 182—193° under 13·6 mm. pressure. When sparteinetrimethylammonium hydroxide is heated at 200—210°, it decomposes, yielding trimethylamine and *hemisparteilene*, $C_{15}H_{23}N$, which boils at 135—155° under 13 mm. pressure.

Taking into consideration the facts already established with regard to the chemistry of sparteine (*loc. cit.*), and accepting the view of Willstätter and Marx that the alkaloid is not a tropane derivative (compare Wackernagel and Wolffenstein, Abstr., 1904, i, 917), it is probable that sparteine has the constitution

$$\begin{array}{lllll} CH_2 & \text{———} & CH_2 \quad CH_2 & \text{———} & CH_2 \\ | & & | \qquad\quad | & & | \\ CH{\cdot}CH_2{\cdot}CH_2{\cdot}N & & \qquad\quad N{\cdot}CH_2{\cdot}CH_2{\cdot}CH\,. & & \\ | & & | \qquad\quad | & & | \\ CH_2 & \text{———} & CH{\cdot}CH_2{\cdot}CH & \text{———} & CH_2 \end{array}$$

The location of the linking methylene group is deduced from the fact that sparteine yields two stereoisomeric methiodides (this vol., i, 608), and must therefore have a constitution analogous to those of conhydrine and conicine (compare Scholtz, Abstr., 1904, i, 1044).

T. A. H.

Alkaloids of some Solanaceæ which induce Mydriasis. Ernst Schmidt (*Arch. Pharm.*, 1905, **243**, 303—309).—This paper for the most part is introductory to those of which accounts are given in the following abstract and this vol., ii, 648.

Datura Mètel has been shown to contain scopolamine (hyoscine) as almost the only constituent of alkaloidal nature; this may be of practical importance, as the plant is easily cultivated.

Datura arborea also contains scopolamine as the main alkaloid, but some hyoscyamine is also present.

Atropa belladonna contains hyoscyamine as almost the only alkaloid in all parts of the plant; the amount found was about 0·8 per cent. in the cultivated plant, 0·4 in that growing wild.

C. F. B.

Alkaloids from certain Species of Datura which induce Mydriasis. Adolf Kircher (*Arch. Pharm.*, 1905, **243**, 309—328).—The leaves of *Datura Metel* contain 0·55, the seeds 0·50 per cent. of alkaloids, reckoned as scopolamine, which forms the bulk of them; small quantities of hyoscyamine and atropine are present also.

The leaves of *Datura quercifolia* contain 0·42, the seeds 0·29 per cent. of alkaloids. In the leaves, stems, unripe fruits, and roots, scopolamine and hyoscyamine are present in about equal proportions; in the seeds, hyoscyamine greatly predominates.

All parts of *Datura arborea* (*D. suaveolens, Brugmansia candida*) contain scopolamine; a small amount of hyoscyamine was found also in the stem and root, of which alone a considerable quantity was available for examination.

Datura stramonium contains mainly hyoscyamine. Confirmation was obtained of Feldhaus' discovery (*Inaug. Diss., Marburg*, 1903) that the percentage of alkaloid in the medial rib and stem of the leaf of the growing plant diminishes gradually after the rest of the leaf has been removed; the greatest diminution observed was from 0·80 to 0·50 per cent. in eight days. C. F. B.

Preparation of 1-Phenyl- and *p*-Tolyl-naphthylamine-8-sulphonic Acid. Aktien-Gesellschaft für Anilin-Fabrikation (D.R.-P. 158923).—When α-naphthylamine-4 : 8-disulphonic acid is

heated with aniline or *p*-toluidine, with the addition of benzoic acid or aniline hydrochloride, for thirty hours at 180°, the phenyl or *p*-tolyl enters the amino-group, the sulphonic group in the 4-position being at the same time replaced by hydrogen, so yielding 1-phenyl- (or *p*-tolyl-) naphthylamine-8-sulphonic acid. Other naphthylaminesulphonic acids do not react in this way. C. H. D.

Compounds of Ketones with Ammonia. Benzophenone Ammonia (Iminobenzophenone). CARL THOMAE (*Arch. Pharm.*, 1905, **243**, 395—398. Compare this vol., i, 509).—A mixture of benzophenone with three times its weight of alcohol is saturated with gaseous ammonia and allowed to remain for several weeks in the dark. It is then exposed in a thin layer for evaporation. Finally the solid residue is powdered, and is either dissolved in ether and treated with an ice-cold saturated ethereal solution of hydrogen chloride, or is dissolved in chloroform, treated with a solution of hydrogen chloride in chloroform, and diluted with benzene. In both cases a white salt separates, which has the composition of iminobenzophenone hydrochloride, $CPh_2{:}NH,HCl$ (Hantzsch and Kraft, Abstr., 1892, 338). By adding an ethereal solution of picric acid to the solution of the crude product in ether, a *picrate* melting at 170° is obtained. A hydrobromide is obtained as an oily by-product of the action of bromine on the base in ethereal solution. These salts are unstable, especially in the presence of water, decomposing into benzophenone and ammonium salts. C. F. B.

New Indoline Bases. ALOIS PLANGGER (*Monatsh.*, 1905, **26**, 833—838. Compare Brunner, Abstr., 1900, i, 360).—3 : 3 : 7-*Trimethyl-2-methyleneindoline hydriodide*, $C_{12}H_{16}NI$, formed by treating the *o*-tolylhydrazone of methyl *iso*propyl ketone with alcoholic hydrogen iodide, crystallises in needles and melts at 185·5°. An impure *stannochloride* of the base, crystallising in long needles, is obtained by boiling the hydrazone with stannous chloride and alcoholic hydrogen chloride in a reflux apparatus. The free *base*, $C_7H_6{<}{\substack{CMe_2\\NH}}{>}C{:}CH_2$, liberated from the double salt by potassium hydroxide, is a yellow oil which boils at 158° under 20 mm. pressure, is volatile in a current of steam, and becomes brown on exposure to the air. The yellow, crystalline *picrate* melts and decomposes at 174°. When warmed with methyl iodide, the base forms the *hydriodide* of 1 : 3 : 3 : 7-tetramethyl-2-methyleneindoline, $C_{13}H_{18}NI$, which crystallises in white leaflets, melts and decomposes at 212°, and when treated with potassium hydroxide yields the *base* $C_7H_6{<}{\substack{CMe_2\\NMe}}{>}C{:}CH_2$. This is a colourless liquid which boils at 138° under 20 mm. pressure, becomes carmine on exposure to air, and forms crystalline salts. The *picrate* crystallises in lemon-yellow needles and melts at 165°; the *ferrichloride* forms whitish-brown, delicate needles melting at 113°, and is insoluble in concentrated hydrochloric acid. G. Y.

3-Ethylindole and 1 : 3 : 3-Triethyl-2-ethylideneindoline. GIUSEPPE PLANCHER and ORESTE CARRASCO (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 31—36).—3-Ethylindole, $C_6H_4<\substack{NH \\ CEt}>CH$, prepared by the condensation of *n*-butaldehydephenylhydrazone in absolute alcoholic solution by means of zinc chloride, has a fæcal odour and crystallises from light petroleum in colourless scales melting at 43° (compare Pictet and Duparc, Abstr., 1888, 370). The picrate, $C_{10}H_{11}N,C_6H_3O_7N_3$, separates from a mixture of benzene and light petroleum in crystals melting at 114—115°; Pictet and Duparc (*loc. cit.*) gave the melting point 143°. 1 : 3 : 3-*Triethyl*-2-*ethylideneindoline*, $C_6H_4<\substack{NEt \\ CEt_2}>C:C_2H_4$, obtained, together with 2 : 3 : 3-triethylindolenine, by the action of ethyl iodide on 3-ethylindole, boils at 187° under 40 mm. pressure, and has a faint sweetish aminic odour; it is colourless, but rapidly turns red. Its *picrate*, $C_{16}H_{23}N,C_6H_3O_7N_3$, separates from alcohol in crystals melting at 102—103°. T. H. P.

Relation between Quinonehydrazones and *p*-Hydroxyazo-compounds. II. New Class of Hydroxyazo-compounds. WALTHER BORSCHE and K. A. OCKINGA (*Annalen*, 1905, 340, 85—109). Compare Abstr., 1904, i, 1056).—Unlike the naphthaquinones, the quinones of the benzene series will not condense with aromatic hydrazines; with *as*-acylphenylhydrazines and semicarbazide, on the other hand, condensation does take place, but not with *as*-phenylalkylhydrazines. The products obtained by using formyl-, hippuryl-, and benzoylhydrazines have been studied; in all cases they behave as hydroxyazo-compounds, since they condense neither with hydroxylamine nor with a second molecule of the hydrazine.

Formylazo-p-*hydroxybenzene*, $OH\cdot C_6H_4\cdot N_2\cdot CHO$, prepared by treating benzoquinone with a solution of formylhydrazine in $N/1$ hydrochloric acid, crystallises in yellowish-brown needles melting and decomposing at 141—142°. 1-*Formylazo*-4-*hydroxy*-3-*methylbenzene*, $OH\cdot C_6H_3Me\cdot N_2\cdot CHO$, prepared from toluquinone, crystallises in yellow needles melting and decomposing at 168—169°. 1-*Formylazo*-4-*hydroxynaphthalene*, prepared from α-naphthaquinone, is a brown, crystalline powder decomposing at 225°. 2-*Formylazo*-1-*hydroxynaphthalene*, prepared from β-naphthaquinone, crystallises in pale brown needles melting and decomposing at 168°.

Hippurylazo-p-*hydroxybenzene*, $OH\cdot C_6H_4\cdot N_2\cdot CO\cdot CH_2\cdot NHBz$, prepared from hippurylhydrazine hydrochloride and benzoquinone in dilute aqueous solution, is a reddish-yellow, crystalline powder, decomposing at 170°. 1-*Hippurylazo*-4-*hydroxy*-3-*methylbenzene*, prepared from toluquinone, forms pale yellow crystals melting at 169—170°. 1-*Hippurylazo*-4-*hydroxy*-2-*methyl*-5-iso*propylbenzene*, prepared from thymoquinone, crystallises in yellow needles melting and decomposing at 200°. 1-*Hippurylazo*-4-*hydroxynaphthalene*, prepared from α-naphthaquinone, crystallises in pale yellow needles melting at 229°. 2-*Hippurylazo*-1-*hydroxynaphthalene* crystallises in orange-red needles melting at 180—181°.

Benzoylazo-p-*hydroxybenzene*, prepared from benzoquinone and a

dilute solution of benzoylhydrazine hydrochloride, forms brown crystals melting and decomposing at 143—144°; it is reduced by phenylhydrazine to s-*benzoyl*-4-*hydroxyphenylhydrazine*, $OH\cdot C_6H_4\cdot NH\cdot NHBz$, which crystallises in needles melting and decomposing at 154°. The benzoylazo-compound forms an *additive compound* with benzenesulphinic acid, $OH\cdot C_6H_4\cdot N(SO_2Ph)\cdot NHBz$, a white, crystalline powder melting at 102°. 1-*Benzoylazo*-3 : 5-*dibromo*-4-*hydroxybenzene*, prepared by bromination of benzoylazo-*p*-hydroxybenzene in acetic acid solution, crystallises in orange-red needles melting at 205°, and when treated with sodium hydroxide is decomposed, yielding 2 : 6-dibromophenol. 2 : 6-*Dibromophenyl benzoate*, prepared by the action of benzoyl chloride on the corresponding phenol in the presence of pyridine, crystallises in leaflets melting at 68°. 1-*Benzoylazo*-4-*hydroxy*-3-*methylbenzene*, prepared from toluquinone, crystallises in pale brown needles melting at 172—174°, and is reduced by phenylhydrazine to s-*benzoyl*-4-*hydroxy*-3-*methylphenylhydrazine*, which is a crystalline powder melting at 175°, and with benzenesulphinic acid forms an *additive product*, a colourless solid melting at 84°. 4-*Benzoylazo*-3-*methylphenyl benzoate*, prepared by benzoylation of the benzoylazo-*o*-cresol in the presence of pyridine, is a pale brown solid. 1-*Benzoylazo*-5-*bromo*-4-*hydroxy*-3-*methylbenzene*, prepared by brominating benzoylazo-*o*-cresol, crystallises in pale yellow needles melting at 209°. 1-*Benzoylazo*-4-*hydroxy*-2-*methyl*-5-iso*propylbenzene*, prepared from thymoquinone, forms dark yellow needles melting at 165—167°, and is reduced by phenylhydrazine to the corresponding *hydrazo*-compound, a crystalline powder melting at 167°. The azo-compound forms an *additive compound* with benzenesulphinic acid, melting at 130°.

On brominating benzoylazothymol, 1-*benzoylazo*-3-*bromo*-4-*hydroxy*-2-*methyl*-5-iso*propylbenzene* is obtained as pale yellow crystals melting at 209°. 1-*Benzoylazo*-4 *hydroxynaphthalene*, prepared from α-naphthaquinone, crystallises in yellow needles melting at 220°, whilst the corresponding *derivative* of β-naphthaquinone forms dark red crystals melting at 180—182°. K. J. P. O.

[Azine Derivatives of Anthraquinone.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 158287).—On heating 2-chloro- or 2-bromo-1-aminoanthraquinone or their derivatives with metallic salts, such as cupric chloride or zinc chloride and sodium acetate in nitrobenzene or other indifferent solvent, condensation takes place, hydrogen chloride or bromide being removed and two anthraquinone groups combining to form an azine. The products form blue or green crystals, and dissolve in boiling aniline or nitrobenzene. Alkaline reducing agents convert them into blue or green dyes. C. H. D.

Some Urazole and Iminothiodiazoline Derivatives. HENRY L. WHEELER and JOANNES G. STATIROPOULOS (*Amer. Chem. J.*, 1905, 34, 117—132).—3-*Ethoxy*-1 : 4-*diphenylurazole*, $NPh<\substack{CO\cdot NPh \\ C(OEt)}>N$, obtained by the action of ethyl iodide on the silver derivative of 1 : 4-diphenylurazole, crystallises in long, slender prisms, softens at

83—85°, melts at 85—86°, and is identical with the compound regarded by Wheeler and Dustin (Abstr., 1901, i, 24) as 5-ethoxy-2-phenylimino-3-phenyloxydiazoline. 1 : 4-*Diphenyl-2-ethylurazole*,

$$NPh<\begin{matrix}CO\cdot NPh\\ |\\ CO\cdot NEt\end{matrix},$$

prepared by the action of ethyl bromide on the sodium derivative of 1 : 4-diphenylurazole at 100°, crystallises in lustrous prisms, melts at 125—126°, and is readily soluble in alcohol, ether, or benzene, and moderately so in hot water.

The additive *compound*, $NHPh\cdot NH\cdot CCl(S\cdot CH_2Ph)\cdot NHPh$, formed by the union of benzyl chloride with diphenylthiosemicarbazide, melts at 149—150°, and is readily soluble in alcohol. The free *diphenyl-ψ-benzylthiosemicarbazide* is very unstable and rapidly oxidises in the air. When an alcoholic solution of the benzyl chloride additive compound, cooled in a freezing mixture, is neutralised with dilute sodium hydroxide, a yellow oil is produced which, after several hours, furnishes bright red needles of the *compound*

$$NPh:N\cdot C(S\cdot CH_2Ph):NPh,$$

melting at about 55°. When an ethereal solution of the free diphenyl-ψ-benzylthiosemicarbazide is treated with carbonyl chloride, 3-*benzylthiol*-1 : 4-*diphenylurazole*, $NPh<\begin{matrix}CO\text{——}NPh\\ C(S\cdot CH_2Ph)\end{matrix}>N$, is produced, which crystallises in long, slender, lustrous needles, melts at 110—112°, and is identical with the substance obtained by Wheeler and Dustin (*loc. cit.*) by the action of benzyl chloride on ethyl *c* : *b*-diphenyl-*a*-thionsemicarbazidate in presence of alkali and regarded as 5-benzylthiol-2-phenylimino-3-phenyloxydiazoline.

5-*Thio-3-ethoxy*-1 : 4-*diphenylurazole*, $NPh<\begin{matrix}CS\cdot NPh\\ C(OEt)\end{matrix}>N$, obtained by the action of phenylthiocarbimide or phenyliminocarbonyl chloride on ethyl phenylthioncarbazinate, crystallises in large, rhombic prisms [$a:b:c = 0{\cdot}9528:1{\cdot}00:1{\cdot}012$], melts at 83°, and is readily soluble in alcohol, less so in ether, and insoluble in water; when boiled with hydrobromic acid, it yields 5-thio-1 : 4-diphenylurazole.

By the action of benzoylthiocarbimide on ethyl phenylthioncarbazinate, Wheeler and Dustin (*loc. cit.*) obtained a compound which melted at 136—138° and was provisionally regarded as 5-thio-4-benzoyl-3-ethoxy-1-phenyltriazolone. It is now found that this substance is 2-benzoylimino-5-ethoxy-3-phenylthiodiazoline,

$$\begin{matrix}NPh\cdot N\\ |\\ NBz:C\text{——}S\end{matrix}>C\cdot OEt.$$

When the compound is boiled with hydrobromic acid, 5-*oxy*-1 : 3-*diphenyltriazole*, $NH<\begin{matrix}CO\text{—}NPh\\ |\\ CPh:N\end{matrix}$, is produced, which crystallises in colourless needles, melts at 229—230°, and is soluble in ether, benzene, or hot alcohol, but only slightly so in boiling water; its constitution was proved by the following synthesis. When benzoylcarbimide is allowed to react with acetonephenylhydrazone, the *semicarbazone*,

$$NHBz\cdot CO\cdot NPh\cdot N:CMe_2,$$

is formed, which crystallises in colourless, microscopic prisms, melts

at 139—140°, and is converted by warm dilute hydrochloric acid into 5-oxy-1 : 3-diphenyltriazole. 5-*Ethoxy*-1 : 3-*diphenyltriazole*,

$$N<\begin{matrix}C(OEt)\cdot NPh\\ CPh{=\!=}N\end{matrix},$$

obtained by the action of ethyl bromide on 5-oxy-1 : 3-diphenyltriazole in presence of potassium hydroxide, crystallises in lustrous, rhombic prisms, melts at 85—86°, and is readily soluble in alcohol, benzene, or ether, and slightly so in boiling water. When 2-benzoylimino-5-ethoxy-3-phenylthiodiazoline is heated at 140—145° in a current of hydrogen chloride, 2-*benzoylimino*-3-*phenylthiodiazolone*,

$$\begin{matrix}NPh\cdot NH\\ NBz{:}C{-\!-\!-}S\end{matrix}>CO,$$

is produced, which crystallises in colourless needles, melts at 206—207°, and is readily soluble in hot alcohol and less so in ether, benzene, or hot water; its *sodium* and *silver* derivatives are described. When either of these derivatives is treated with ethyl iodide, 2-benzoylimino-5-ethoxy-3-phenylthiodiazoline is regenerated. The diazoline may also be obtained by the action of benzoyl *iso*cyanochloride (Johnson and Menge, Abstr., 1904, i, 949) on ethyl phenylthioncarbazinate. Contrary to the statement of Wheeler and Dustin (*loc. cit.*), the compound is not desulphurised by silver nitrate; mercuric oxide is also without effect on it.

The following derivatives of 5-thio-1 : 3-diphenyltriazole (Wheeler and Beardsley, Abstr., 1902, i, 503) are described. 5-*Methylthiol*-1 : 3-*diphenyltriazole*, $N<\begin{matrix}C(SMe)\cdot NPh\\ CPh{=\!=}N\end{matrix}$, crystallises in large, colourless needles, melts at 56—57°, and is readily soluble in ether or benzene, and sparingly so in boiling water. 5-*Ethylthiol*-1 : 3-*diphenyltriazole* forms stout, colourless prisms, melts at 52—53°, and when dissolved in hydrobromic acid yields a *salt* melting at 152°. 1 : 3-*Diphenyltriazole* 5-*disulphide*, $(C_{14}H_{10}N_3)_2S_2$, crystallises in slender, colourless needles, melts at 182—183°, and is slightly soluble in ether or alcohol and insoluble in water.

E. G.

Action of Alkylene Haloids on *m*- and *p*-Dibenzenesulphophenylenediamine. OSCAR HINSBERG and J. KESSLER (*Annalen*, 1905, **340**, 110—121).—It has been shown by Hinsberg and Strupler (Abstr., 1896, i, 47) that diphenylsulphone-*o*-phenylenediamine gives cyclic compounds with methylene chloride, ethylene bromide, and trimethylene bromide. In the case of derivatives of *m*- and *p*-phenylenediamine, it has now been found that such cyclic compounds are not produced, but that substances belonging to a bimolecular type are formed.

Bisdiphenylsulphonemethylene-m-*phenylenediamine*,

$$C_6H_4<\begin{matrix}N(SO_2Ph)\cdot CH_2\cdot N(SO_2Ph)\\ N(SO_2Ph)\cdot CH_2\cdot N(SO_2Ph)\end{matrix}>C_6H_4,$$

is prepared by heating diphenylsulphone-*m*-phenylenediamine with methylene chloride and sodium methoxide in alcohol under pressure at 110°; the compounds can be isolated from the product by repeated precipitation from solution in various solvents as an amorphous,

colourless powder, which becomes coloured at 64° and melts at 82—86° to a turbid liquid, which is clear at 110—120°; it is insoluble in acids and in alkali hydroxides.

Bisdiphenylsulphone-ethylene-*m*-phenylenediamine,

$$C_6H_4{<}{N(SO_2Ph)\cdot CH_2\cdot CH_2\cdot N(SO_2Ph) \atop N(SO_2Ph)\cdot CH_2\cdot CH_2\cdot N(SO_2Ph)}{>}C_6H_4,$$

prepared in a similar manner, is a colourless powder, becoming brown at 85° and melting at 92—96° to a turbid liquid which becomes clear at 120°. The statements previously made regarding this compound (*loc. cit.*) are incorrect. *Bisdiphenylsulphonetrimethylene*-m-*phenylenediamine*, $C_{42}H_{40}O_8N_4S_4$, is an amorphous, colourless powder, becoming brown at 80° and melting at 102—108° to a turbid liquid which becomes clear at 125°. When heated at 150° with concentrated hydrochloric acid, it is converted into an amorphous base. *Bisdiphenylsulphonetrimethylene*-p-*phenylenediamine* is an amorphous, colourless powder, becoming brown at 60° and melting at 75—80° to a turbid liquid which becomes clear at 125°.

Diphenylsulphonediethyl-m-*phenylenediamine*, $C_6H_4(NEt\cdot SO_2Ph)_2$, prepared from diphenylsulphone-*m*-phenylenediamine, ethyl iodide, and sodium ethoxide at 110°, forms colourless crystals melting at 105°; its molecular weight in naphthalene solution is normal.

K. J. P. O.

[Azo-dyes from β-Diketones and β-Ketonic Esters.] FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 158148 and 160040).—Diazotised solutions of *o*-aminosalicylic acid and its substituted derivatives combine with the sodium derivatives of acetylacetone, benzoylacetone, ethyl acetoacetate, acetoacetanilide, and similar compounds, yielding yellow, crystalline dyes. The products form bright yellow lakes, of which the cupric lakes are the most remarkable.

Similar products are obtained when *o*-aminosalicylic acid is replaced by *o*-aminophenol or its substituted derivatives, such as *o*-aminophenolsulphonic acid or 6-nitro-2-aminophenol-4-sulphonic acid.

C. H. D.

Oxidation of *o*-Phenylenediamine. RICHARD WILLSTÄTTER and ADOLF PFANNENSTIEL (*Ber.*, 1905, **38**, 2348—2352. Compare Griess, *J. pr. Chem.*, 1871, [ii], **3**, 142; O. Fischer and Hepp, Abstr., 1889, 499; 1890, 800, 1440; O. Fischer and O. Heiler, Abstr., 1893, i, 266; O. Fischer and O. Jonas, Abstr., 1895, i, 25; O. Fischer, Abstr., 1904, i, 349; Ullmann and Mauthner, Abstr., 1903, i, 199; 1904, i, 192).—Silver oxide and lead peroxide react with an ethereal solution of *o*-phenylenediamine in the absence of moisture yielding a pale yellow solution which presumably contains *o*-quinonedi-imine. When warmed or shaken with hydrochloric acid, the colour of the ethereal solution turns to deep red and then contains diaminophenazine and *o*-azoaniline. These products may be readily separated, as the diaminophenazine is completely removed by shaking the ethereal solution with water.

o-*Azoaniline* (2 : 2′-*diaminoazobenzene*), $N_2(C_6H_4NH_2)_2$, is most readily purified by conversion into the sulphate. The best yields are

obtained by boiling the oxidised ethereal solution for some hours. It crystallises from hot alcohol or benzene in copper-red plates with a metallic lustre and melts at 134°. Dilute solutions have a pale yellow and concentrated solutions a yellowish-red colour. With acids, it gives no characteristic colour changes (compare Nietzki, Abstr., 1884, 740). The *hydrogen sulphate*, $C_{12}H_{12}N_4,2H_2SO_4$, crystallises in long, yellow prisms, and is sparingly soluble in water. o-*Azoacetanilide* forms long, orange-yellow prisms melting at 271°. *o*-Phenylenediamine forms an *additive compound* with silver nitrate, $C_6H_8N_2,AgNO_3$; this is stable in the dry state, but when warmed with water, metallic silver is deposited and diaminophenazine nitrate is formed. J. J. S.

Rate of Decomposition of Diazonium Salts. JOHN C. CAIN (*Ber.*, 1905, **38**, 2511—2517).—Schwalbe's contention (this vol., i, 618) that the conclusions of Cain and Nicoll (Trans., 1902, **81**, 1412) were based on the rate of decomposition of diazonium salts with absolutely pure bases and could not accordingly hold for technical diazo-solutions is incorrect.

The author has now studied the decomposition of benzenediazonium chloride in acetic acid solution; the effect of other acids on the decomposition of diazonium salts has also been examined. Hydrochloric acid in varying concentrations has no influence on the rate of decomposition of benzenediazonium chloride. Sulphuric acid, on the other hand, has an effect when the concentration of the acid is increased, giving rise to a secondary reaction. Equivalent solutions of benzenediazonium chloride, sulphate, nitrate, and oxalate respectively are decomposed at the same rate. A. McK.

Reaction of Aromatic Azo-compounds with Aromatic Amines differing from the Induline Synthesis. ARTHUR WEINSCHENK (*Zeit. Farb. Text. Ind.*, 1905, 4, 337—339).—The action of 1 mol. of azobenzene on 1 mol. of α-naphthylamine in warm 70 to 80 per cent. sulphuric acid solution leads to the formation of benzidine and a *base* which, on treatment with a small quantity of zinc dust in dilute acid solution and precipitation with ammonia, is obtained as a yellowish-white mass, becoming grey on warming or drying in air, and containing C = 82·3; H = 5·8; N = 11·7 per cent. It is easily soluble in dilute sulphuric or hydrochloric, glacial acetic, or hot dilute oxalic acid, but is only slightly soluble in most organic solvents and is almost insoluble in hot dilute acetic acid or water. With acetic anhydride, the base forms an *acetyl* derivative insoluble in dilute acids; with sodium nitrite in hydrochloric acid, it yields an insoluble *polydiazo*-derivative, which, with a further quantity of sodium nitrite, forms a brown *nitrosodiazo*-solution. This combines with 2 mols. of the usual azo-dye components to form derivatives which dye unmordanted cotton-wool. With sodium naphthionate or β-naphthylamine-5-sulphonate in presence of sodium acetate, the nitrosodiazo-solution forms intermediate products, which contain a free diazo-group and form mixed azo-dyes with *H*-acid in alkaline solution. The base derived from azobenzene and α-naphthylamine must contain the group

$NH \cdot C_{10}H_6 \cdot NH_2$. The reaction by which it is formed is capable of extension to other aromatic azo-compounds and aromatic amines.
G. Y.

Tetrazophenolsulphonic Acid. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 158532).—*m*-Phenylenediaminedisulphonic acid is converted by an excess of nitrous acid at 15° into a *tetrazophenolsulphonic acid*, which separates in yellow crystals. One sulpho-group is thus replaced by hydroxyl.
C. H. D.

Colouring Matter of Blood. V. H. Goldmann, J. Hepter, and Leon Marchlewski (*Zeit. physiol. Chem.*, 1905, **45**, 176—182. Compare this vol., i, 399).—The azo-dye previously described is *hæmopyrroledisazobenzene hydrochloride*, $C_{20}H_{22}N_5Cl$. In the powdered state it melts at 233°, and is only sparingly soluble in ether, benzene, or chloroform. Its solution in concentrated sulphuric acid has at first a bluish-violet colour, but this changes to reddish-violet. The solution in alcoholic potash has a more reddish colour. The spectroscopic properties are not specially characteristic. Hæmopyrrole and toluenediazonium chloride yield the *hydrochloride* of an *azo-dye*, $C_{22}H_{26}N_5Cl$, in the form of dark brown, glistening needles melting at 254°.
J. J. S.

State of Combination of Sulphur in Proteids. Paul N. Raikow (*Chem. Zeit.*, 1905, **29**, 900—901).—Twenty grams of carefully washed unbleached wool, placed in a stoppered bottle of 300 c.c. capacity with phosphoric acid of sp. gr. 1·7, becomes brown after sixteen hours, and on removing the stopper a strong odour of sulphur dioxide is noticed. After two months, the contents of the bottle are changed to a dark brown, thick, homogeneous liquid and evolve a very powerful odour of sulphur dioxide; only a very small additional amount is formed on setting aside the bottle for a few more days In the author's opinion, this proves that part of the sulphur in keratin is combined directly with oxygen. Human hair behaves in much the same way as wool, although the action is somewhat slower. One gram of each of the following substances, sulphuric acid, potassium methyl sulphate, sulphanilic acid, and the mono- and di-sulphonic derivatives of salicylic acid, allowed to remain for ten days in stoppered bottles with 20 c.c. of phosphoric acid, did not in any case evolve sulphur dioxide. The conclusion is reached that the sulphur in the proteid molecule is not combined in the form of a sulphate or a sulphonic acid, but more probably is present in part in a sulphite-like form.
P. H.

Oxidations with Calcium Permanganate. Reply to Kutscher and Seemann. Richard Burian (*Zeit. physiol. Chem.*, 1905, **45**, 351—354. Compare Abstr., 1904, i, 127; this vol., ii, 271).—Polemical.
J. J. S.

Fibrinoglobulin. Wolfgang Heubner (*Zeit. physiol. Chem.*, 1905, **45**, 355—356).—A reply to Huiskamp (this vol., i, 499). It is

probable that Huiskamp's fibrinoglobulin solutions contained albumins and fibrinogen unless they were prepared by Hammarsten's method with neutral plasma. J. J. S.

Substances Extracted from Muscle. II. Carnitine. WLADIMIR VON GULEWITSCH and R. KRIMBERG (*Zeit. physiol. Chem.*, 1905, **45**, 326—330. Compare Abstr., 1900, i, 516).—A new base, *carnitine*, is precipitated by the addition of potassium bismuth iodide solution to the filtrate from the precipitation of carnosine as its silver derivative. It has been obtained as the *platinichloride*, $C_{14}H_{32}O_6N_2Cl_6Pt$, in the form of minute, orange-red needles which melt and decompose at 214—218°. The base is strongly alkaline and dissolves readily in water, as do also the *hydrochloride* and *nitrate*. The latter crystallises in needles and has $[\alpha]_D$ about $-22°$. J. J. S.

Isolation of Lysine. ERNST WINTERSTEIN (*Zeit. physiol. Chem.*, 1905, **45**, 77—78).—Lysine is precipitated by mercuric chloride in the presence of barium hydroxide. In the separation of lysine from arginine and histidine, the latter are precipitated by the addition of silver nitrate and baryta, the excess of silver is removed from the filtrate, and the lysine precipitated by the addition of mercuric chloride. To obtain the base, the well-washed precipitate is suspended in dilute hydrochloric acid and decomposed with hydrogen sulphide. The filtrate when evaporated leaves the base as a syrup. J. J. S.

Peptones. WALTER NEUMANN (*Zeit. physiol. Chem.*, 1905, **45**, 216—251. Compare Siegfried, Abstr., 1903, i, 782).—The molecular conductivities of aqueous solutions of pepsin-fibrinpeptone-α, of antipeptone-α, and of antipeptone-β have been determined, but, as with certain other amphoteric electrolytes, dissociation constants cannot be obtained by Ostwald's dilution law. The concentration of the hydrogen ions in aqueous solutions of peptones has been determined by Löwenherz' method (Abstr., 1896, ii, 587). The results indicate that a $N/16$ solution of pepsin-fibrinpeptone is only $0·0002N$ as regards hydrogen ions, whereas a $N/16$ solution of acetic acid is $0·00105N$ as regards hydrogen ions.

The peptones themselves in aqueous solution can precipitate gold from its colloidal solutions.

The equivalents of certain acids have been determined by mixing a given volume of the acid solution of known concentration with the same volume of much more dilute standard alkali hydroxide and determining the specific conductivity of the partially neutralised solution; to the mixture is added its own volume of the alkali solution and the conductivity again determined. The operation is repeated and the results plotted in the form of a curve of which the co-ordinates represent specific conductivities and concentration of the acid. With a strong acid and strong base, the curve consists of two straight lines meeting at a eutectic point which represents the equivalent weight of the acid. With a weak acid or alkali, a hyperbolic curve is given, one limb of which runs practically parallel with the concentration co-ordinate. In this case, the equivalent of the acid is given by the

point of intersection of the asymptotes to the curve. The method has been tried for telluric acid, glycine, and asparagine, using sodium hydroxide solutions of different concentrations, and also for creatine, glycine, and asparagine, as bases using hydrochloric acid of known strength.

In the latter experiments, the values obtained are rather high, especially with the more dilute solutions, owing to the high degree of hydrolysis. The same method has been used for determining the equivalents of some of Siegfried's pure peptones, using both sodium hydroxide and also hydrochloric acid solutions. The numbers obtained are:

	With NaOH.	With HCl.	Ratio.
Pepsin-fibrinpeptone-*a*	248	370	2 : 3
Pepsin-glutinpeptone-*a*	320	470	2 : 3
Antipeptone-*a*	157	290	1 : 2
Antipeptone-*β*	197	397	1 : 2

It is thus probable that the antipeptones are dibasic acids, but monoacidic bases, and the other two peptones tribasic acids and diacidic bases.

A discussion of probable molecular weights of certain peptones follows.

The numbers previously obtained by Calvert (Trans., 1902, **81**, 10) indicate that in dilute solutions hydrogen peroxide behaves as a monobasic acid and gives salts of the type $NaHO_2$. J. J. S.

Peptones. MAX SIEGFRIED (*Zeit. physiol. Chem.*, 1905, **45**, 252—257. Compare preceding abstract).—When aspartic and glutamic acids are treated with a slight excess of barium hydroxide and carbon dioxide passed into the solution until it is faintly acid, then boiled and evaporated in a platinum dish, barium hydrogen salts of the type $[CO_2H\cdot CH(NH_2)\cdot CH_2\cdot CO_2]_2Ba$ are obtained. The peptones yield barium salts in a similar manner, and it should follow that these are acid salts, and the equivalents determined from the barium salts must thus be greater than those from the titration and conductivity method, but the two should bear a simple relationship. This is shown to hold good for trypsin-fibrinpeptones-*a* and -*β*, pepsin-fibrinpeptone-*a* and pepsin-glutinpeptone. J. J. S.

Proteids obtained from Ricinus Seeds. ERNST WINTERSTEIN (*Zeit. physiol. Chem.*, 1905, **45**, 69—76).—The proteid extracted from *Ricinus* seeds by Ritthausen's method contains only 13·6 per cent. of nitrogen, and when hydrolysed with concentrated hydrochloric acid yields various bases. A new base isomeric with lysine has been isolated from the lysine fraction. The *dihydrochloride* of the new base is insoluble in boiling methyl alcohol. It sinters at 155°, melts at 160°, and decomposes at 162°; it is optically active and has $[\alpha]_D$ $+12{\cdot}9°$. It yields no precipitates with picric acid, gold chloride, platinic chloride, mercuric chloride or sulphate, tannic acid, or potassium mercuri-iodide. With phosphotungstic acid, it yields a white precipitate which dissolves on warming; with phosphomolybdic acid a

yellow precipitate, with Nessler's reagent a white precipitate, and a similar one with mercuric chloride and alkali hydroxide. Its most characteristic reaction is the glistening, dark red, crystalline precipitate yielded with potassium bismuth iodide. The amount of the new base is extremely small; from 200 grams of proteids only 0·3 gram of the hydrochloride was obtained, and the amount appears to vary with different samples of seeds. J. J. S.

Cause of the Fluorescent Reaction of Bile Acids with Sulphuric Acid. FRITZ PREGL (*Zeit. physiol. Chem.*, 1905, **45**, 166—175).—When dry cholic acid is heated with glacial acetic and concentrated sulphuric acids, a product is obtained from which two substances have been isolated: (1) a colourless acid insoluble in water but soluble in sulphuric acid to a non-fluorescent solution, and (2) a neutral substance, *dehydrocholone*, $C_{24}H_{28}O$ or $C_{23}H_{27}O$, which dissolves in concentrated sulphuric acid, yielding an orange-red solution with a green fluorescence. It is readily soluble in most organic solvents, but insoluble in water, acids, or alkalis. It has not been obtained in a crystalline form, melts at 90—100° to a brown, transparent liquid, and with nitric acid yields a dinitrodicarboxylic acid.

An examination of the molecular refraction and dispersion of cholic acid leads to the conclusion that no ethylenic (or benzene) linkings are present in the molecule, whereas with dehydrocholone the presence of such linkings is highly probable. The heat of combustion of cholic acid is 8103 cal. per gram. J. J. S.

Philothionic Hydrogen. JOSEPH DE REY-PAILHADE (*Bull. Soc. chim.*, 1905, [iii], **33**, 850—854. Compare Abstr., 1904, i, 837).—When pseudo-philothion is heated at 120—130° for some fifteen hours it loses the property of being able to reduce sulphur; this is attributed to the action of the atmospheric oxygen on the philothionic hydrogen. When dry pseudo-philothion is heated with sulphur at 120° for four hours, hydrogen sulphide is formed in quantity, but if the experiment is repeated while a slow stream of air is passed over it, only traces of sulphide are formed.

At the ordinary temperature, the philothion from ovalbumin is not readily destroyed by atmospheric oxygen, does not decolorise sodium indigotinsulphonate, or methylene-blue, and is only very slowly acted on by hydrogen peroxide at the ordinary temperature. Boiling with acidified hydrogen peroxide destroys philothion, as does nitrous acid. The question of the presence of hydrogen sulphide in various foods is discussed. J. J. S.

Organic Chemistry.

Nature of the Carbon Double Linking. HUGO BAUER (*J. pr. Chem.*, 1905, [ii], **72**, 201—210. Compare Abstr., 1904, i, 841).—The addition of bromine to unsaturated carbon compounds is affected by the presence of chlorine atoms and of nitrile groups in the same manner as by that of phenyl or carboxyl groups or of bromine atoms. Tetrachloroethylene, $CCl_2{:}CCl_2$, and dichlorostilbene,

$$C_6H_5{\cdot}CCl{:}CCl{\cdot}C_6H_5,$$

for example, do not form additive compounds with bromine. The nitrile group affects the addition of bromine to a greater extent than does the carboxyl group, whilst this has a greater effect than the phenyl group. Thus, α-phenylcinnamonitrile, $CHPh{:}CPh{\cdot}CN$, forms a dibromide, but ethyl benzylidenemalonate, $CHPh{:}C(CO_2Et)_2$, decolorises bromine to only a slight extent, and α-cyanocinnamic esters, $CHPh{:}C(CN){\cdot}CO_2R$, do not unite with bromine. The tendency to add bromine diminishes as the negative nature of the substituting groups increases; thus addition of bromine is no longer possible if a nitro-group is introduced into the para-position in either of the phenyl groups of α-phenylcinnamonitrile; if the nitro-group is introduced into an ortho-position, the behaviour of the resulting product resembles that of ethyl benzylidenemalonate, whilst a nitro-group in the meta-position has no influence on the behaviour towards bromine.

If unsaturated carbon compounds with one double linking are considered to contain two tervalent carbon atoms which become quadrivalent on formation of additive compounds, carbon forms an exception to the general rule that elements act with higher valencies the more negative the groups or atoms to which they are attached. The protection of a double linking by neighbouring negative groups explains the formation of 3 : 4- instead of 1 : 4-dibromo-additive compounds from such substances, containing conjugated ethylene linkings, as *p*-nitrophenylcinnamenylacrylic acid,

$$CHPh{:}CH{\cdot}CH{:}CH(C_6H_4{\cdot}NO_2){\cdot}CO_2H,$$

and cinnamylidenemalonic esters, $CHPh{:}CH{\cdot}CH{:}C(CO_2R)_2$. To the negative influence of the substituting groups are due such cases, as with *s*-diphenylethylene, in which bromine is added, but the additive compound immediately loses hydrogen bromide and forms an unsaturated compound, as also certain cases of intramolecular change, for example, that of cyanoform,

$$CH(CN)_2{\cdot}C{:}N \longrightarrow C(CN)_2{:}C{:}NH.$$

G. Y.

New Heptane: βδ-Dimethylpentane. G. CHONIN (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 521—523).—Saturation of dimethyl*iso*butylcarbinol with hydrogen iodide yields the corresponding *iodide*, $CHMe_2{\cdot}CH_2{\cdot}CMe_2I$, which boils and decomposes slightly at 140—142° under 756 mm. pressure. When heated with hydriodic acid in a

sealed tube at 220—230°, this iodide is converted into *βδ-dimethylpentane*, $CHMe_2{\cdot}CH_2{\cdot}CHMe_2$, which boils at 83—84° under 764 mm. pressure, has the sp. gr. 0·6971 at 0°/0° and 0·6805 at 20°/0°, and n_D 1·3825 at 20°. T. H. P.

Preparation of Hexachloroethane. KARL A. HOFMANN and E. SEILER (*Ber.*, 1905, **38**, 3058—3059. Compare Kolbe, *Annalen*, **54**, 147; Goldschmidt, *Ber.*, 1881, **14**, 928; Radziszewski, *ibid.*, 1884, **17**, 834).—Carbon tetrachloride is heated with aluminium amalgam at 70° in a reflux apparatus and then poured into twice its volume of ice-water. The unaltered carbon tetrachloride is then distilled off and at 100° hexachloroethane passes over with the steam and may be extracted with ether. From 100 grams of the tetrachloride, 35 grams were recovered and 42 grams of hexachloroethane were obtained. When treated in a similar manner, chloroform deposits carbon, and hydrogen is evolved, whilst aluminium chloride goes into solution. J. J. S.

Oxidising Action of Ferric Chloride in Sunlight. ALFRED BENRATH (*J. pr. Chem.*, 1905, [ii], **72**, 220—227).—A number of substances were mixed with sublimed ferric chloride in a sealed tube and exposed to bright sunlight. Under these conditions methyl alcohol and ferric chloride form methyl chloride, formaldehyde hydrochloride, hydrogen chloride and, if anhydrous, ferrous chloride methyl alcoholate, $FeCl_2,4CH_4O$, but if in presence of moisture, $FeCl_2,4H_2O$. Formaldehyde and ferric chloride in presence of water form formic acid, hydrogen chloride, and ferrous chloride, $FeCl_2,4H_2O$. Trioxymethylene and ferric chloride form an unstable, dark violet additive compound, but no oxidation of the trioxymethylene takes place. The action of ferric chloride on formic acid leads to the formation of carbon dioxide and hydrogen chloride. Absolute ethyl alcohol and ferric chloride yield acetaldehyde, ethyl chloride, hydrogen chloride, and ferrous chloride, $FeCl_2,2H_2O$ or $FeCl_2,4H_2O$, if 95 per cent. alcohol is used. Ether is oxidised to acetaldehyde hydrochloride, hydrogen chloride, and a substance which may be a mixture of butane and ethyl chloride. With anhydrous ether, anhydrous ferrous chloride, but in presence of water $FeCl_2,4H_2O$, is formed. In presence of water, acetaldehyde is oxidised to acetic acid, hydrogen chloride and ferrous chloride, $FeCl_2,4H_2O$, being formed; but if anhydrous substances are used, the aldehyde is converted into resin.

Acetic acid and ferric chloride form a rose-red powder. The action of ferric chloride on dimethylethylcarbinol is that of a dehydrating agent. G. Y.

Spontaneous Oxidation of Ethyl Alcohol. L. MATHIEU (*Chem. Centr.*, 1905, ii, 782; from *Bull. Assoc. Chim. Sucr. Dist.*, 1905, **22**, 1283—1293).—Aldehyde is formed in wines and other alcoholic liquids of similar concentration by simple contact with the air without the interaction of porous substances or micro-organisms.

The process is accelerated by the presence of oxidisable substances, such as sulphur dioxide, ferrous sulphate, ferrous oxide, manganous oxide, &c. Sunlight has the same effect, and green glass containing-vessels favour the oxidation. The phenomenon is subjected to a theoretical discussion. H. M. D.

Action of Stannic and Titanic Chlorides on Organic Hydroxyl Compounds. ARTHUR ROSENHEIM and RICHARD SCHNABEL (*Ber.*, 1905, **38**, 2777—2782. Compare Pfeiffer, this vol., ii, 594).—Compounds of the type $SnCl_2(OMe)_2,HCl$, $SnCl_2(OEt)_2,HCl$,

$$SnCl_2(OPr)_2,HCl,$$

and $SnCl_2(OPh)_2,HCl$ have been obtained by the addition of stannic chloride to an excess of the well-cooled alcohol and partial evaporation of the solution. The compounds are all colourless, crystalline, and hygroscopic. The *propyl* compound melts at 163°. With alcohol in a good freezing mixture, stannic chloride yields the compound $SnCl_4,2EtOH$.

Stannic chloride reacts with a hot chloroform solution of salicylic acid yielding the crystalline product $SnCl_2(O{\cdot}C_6H_4{\cdot}CO_2H)_2,HCl$, which melts at 150°. It is relatively stable and readily soluble in alcohol. With pyridine, the salt $SnCl_2(O{\cdot}C_6H_4{\cdot}CO_2H)_2,2C_5NH_5$ is obtained, and the complex $SnCl_2(O{\cdot}C_6H_4{\cdot}CO_2H)_2$ has thus an amphoteric character.

Pfeiffer's compounds are also regarded as hydrochlorides.

The following compounds have been obtained from titanic chloride: $TiCl(OPr)_3,HCl$; $TiCl(O{\cdot}C_6H_4{\cdot}CO_2H)_3,HCl$ (compare Demarcay, *Compt. rend.*, 1874, **80**, 51). With the bromide, similar compounds, for example, $TiBr(O{\cdot}C_6H_4{\cdot}CO_2H)_3,HBr$, have been prepared. The compounds react with pyridine in alcoholic solution, yielding

$$TiO(O{\cdot}C_6H_4{\cdot}CO_2H)_2,2C_5NH_5.$$

J. J. S.

Sodium Derivatives of Normal Propylene Glycol. ERNESTO PARONE (*Chem. Centr.*, 1905, ii, 751; from *Boll. Chim. Farm.*, 1905, **44**, 481—483).—To obtain the mono-sodium compound, propylene glycol is treated with sodium amalgam, the product warmed with amyl alcohol, dissolved in boiling ethyl alcohol, and the solution distilled in a current of hydrogen. On cooling the residual solution, crystals of the formula $C_3H_7O_2Na,EtOH$ separate. This substance deliquesces in the air and gradually decomposes, but can be kept in a sealed tube filled with hydrogen. When heated at 170° under diminished pressure, it gradually loses ethyl alcohol and a white porous mass remains.

The di-sodium compound, $C_3H_6O_2Na_2$, is obtained by adding gradually sodium dissolved in alcohol to a solution of the mono-sodium compound in alcohol and heating for three hours in a current of hydrogen.

Another method consists in treating a solution of the glycol in absolute alcohol with sodium ethoxide. The former method gives a 23, the latter a 94 per cent. yield. Hard, white, porous, hygroscopic masses are obtained, which decompose at 210—245° and must be kept in an atmosphere of hydrogen. H. M. D.

Ketonic Alcohols. ANDRÉ KLING (*Ann. Chim. Phys.*, 1905, [viii], **5**, 471—559).—For the most part a *résumé* of work already published (Abstr., 1899, i, 323; 1900, i, 129; 1901, i, 625; 1903, i, 138, 223; 1904, i, 2, 133, 474; this vol., i, 3, 172, 327, 503, 504, 625).—Acetylcarbinyl formate has a sp. gr. 1·1322 at 15°/15° and n_D 1·4206 at 15°. The *propionate* boils at 152—156° and yields a *hydrazone* melting at 189—190°. The *stearate* crystallises in unctuous scales, melts at 49—50°, and is soluble in alcohol and ether, slightly so in water.

Attempts were made to determine the velocity of esterification of acetylcarbinol by acetic acid, but these had to be abandoned owing to the difficulty of titrating the free acetic acid in presence of acetylcarbinol, which behaves as a pseudo-acid: the initial velocity appears to be about 3·98.

Neither acetylcarbinol nor acetylmethylcarbinol is fermented by *Mycoderma aceti*, yeast, or *Aspergillus niger*, but *Penicillium glaucum* darkens the colour of a solution of acetylmethylcarbinol and induces a dextrorotation, which reaches a maximum and eventually disappears (at the same time as the ketone alcohol) if the fermentation is allowed to proceed for a long enough period.

Benzoylcarbinol, prepared by heating bromoacetophenone with potassium formate and methyl alcohol in a closed tube, behaves towards reducing and oxidising agents in a manner precisely analogous with that of the aliphatic ketone-alcohols. It differs from them principally in not being obtainable by the biological oxidation of the corresponding glycol. T. A. H.

Condensation of Aldehydes with Ketones in Presence of Potassium Cyanide. JULIUS SALKIND (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 484—492. Compare Claisen, Abstr., 1899, i, 667).—*Methylpentanonol* [*γ-keto-αβ-dimethylbutyl alcohol*],

$$CH_3{\cdot}CO{\cdot}CHMe{\cdot}CHMe{\cdot}OH,$$

prepared by the condensation of methyl ethyl ketone with acetaldehyde in presence of potassium cyanide, boils at 82—83° under 16 mm., at 74—75° under 10 mm., and at 186—188° under the ordinary pressure, and has the sp. gr. 0·9779 at 0°/4° and 0·9651 at 17°/4°. The *semicarbazone*, $C_7H_{15}O_2N_3$, melts at 172·5—173° and dissolves moderately readily in alcohol or water. On reduction with sodium amalgam, methylpentanonol yields the corresponding *glycol*, $OH{\cdot}CHMe{\cdot}CHMe{\cdot}CHMe{\cdot}OH$, which boils at 103—105° under 10 mm., at 113—115° under 20 mm., and at 211—212° under the ordinary pressure, and has the sp. gr. 0·9762 at 0°/4° and 0·9628 at 18°/4°. Oxidation of methylpentanonol with permanganate yields almost exclusively acetic acid (compare Zelinsky and Zelikoff, Abstr., 1901, i, 657).

Dimethylpentanonol [*γ-keto-αββ-trimethylbutyl alcohol*],

$$CH_3{\cdot}CO{\cdot}CMe_2{\cdot}CHMe{\cdot}OH,$$

prepared by the condensation of methyl *iso*propyl ketone with acetaldehyde in presence of potassium cyanide, boils at 79—80° under 10 mm. pressure and has the sp. gr. 0·9786 at 4°/0° and 0·9676 at 13·5°/4°. The *semicarbazone*, $C_8H_{17}O_2N_3$, separates in stellar, crys-

talline aggregates melting at 127°, and dissolves readily in alcohol, water, or acetone. Oxidation of dimethylpentanonol with chromic acid in acetic acid solution yields dimethylacetylacetone, which was identified by means of its *disemicarbazone*, $C_9H_{18}O_2N_6$, melting at 227—228°. T. H. P.

Compounds of Gold with Organic Sulphur Groups. Felix Herrmann (*Ber.*, 1905, **38**, 2813—2825).—When 3 mols. of a mercaptan are added to an alcoholic solution of 1 mol. of auric chloride, the auric mercaptide is formed as a brown precipitate which becomes white, whilst the colourless filtrate contains hydrochloric acid and the disulphide corresponding with the mercaptan.

Aurous iso*amylmercaptide*, $Au{\cdot}SC_5H_{11}$, forms a cryptocrystalline powder which is stable on exposure to air or light, decomposes at about 150°, with formation of metallic gold and an oily distillate, and is sparingly soluble in boiling toluene. *Aurous benzylmercaptide*, $Au{\cdot}SC_7H_7$, decomposes at 190—200° and is almost insoluble in boiling toluene. The action of 2 mols. of dibenzyl sulphide on 1 mol. of auric chloride or ammonium aurichloride in alcoholic or ethereal solution leads to the formation of a voluminous, orange precipitate, consisting of spherical aggregates of needles, which changes after some days, or quickly on warming, into *aurodibenzylsulphine chloride*, $AuS(C_7H_7)_2Cl$, which is obtained as a heavy, crystalline powder. This is dimorphous, and crystallises from its hot saturated solution in alcohol or chloroform, on cooling in tetragonal needles, or on slow evaporation of its solutions at temperatures below 25° in monoclinic crystals resembling rhombohedra. It melts and decomposes at 122°, and becomes yellow on exposure to air, or violet in absence of air and light; in chloroform solution it yields, with hydrogen sulphide, a precipitate of auric sulphide, with mercaptans, precipitates of aurous mercaptides, and with potassium cyanide, benzyl sulphide and potassium auricyanide. The action of potassium iodide on auric dibenzylsulphine chloride leads to the production of benzyl sulphide, metallic gold, and potassium aurichloride and chloride; of silver nitrate, to the formation of aurous oxide, silver chloride, gold, and benzyl sulphide; of aqueous or alcoholic ammonia, to the formation of auriamine chloride, $AuNH_3Cl$. This is obtained as a white, cryptocrystalline precipitate, decomposes at 150—200°, and is formed also by the action of aqueous ammonia on auric chloride.

Auric dibenzyl sulphide dichloride, $S(C_7H_7)_2{:}AuCl_2{\cdot}AuCl_2{:}S(C_7H_7)_2$?, which is the intermediate product in the formation of aurodibenzylsulphine chloride, is obtained by the action of 3 mols. of benzyl sulphide on 2 mols. of auric chloride in ethereal solution. It crystallises in delicate, glistening, orange needles, is stable when exposed to light or air, melts and decomposes at 127°, and dissolves in boiling chloroform to form a yellow solution, but is only sparingly soluble in ether or alcohol. On addition of alcoholic ammonia to the chloroform solution, it forms an amorphous precipitate which, when dry, explodes on being heated; with hydrogen sulphide, it forms a black precipitate of auroauric sulphide, and when treated with alcoholic potassium hydroxide yields a black precipitate of metallic gold. The action of

chlorine on auric dibenzyl sulphide chloride in chloroform solution leads to the formation of a yellow solution, whilst with bromine a *product*, $AuBr(Cl)\cdot S(C_7H_7)_2$?, is obtained, which crystallises in dark red needles.

The ethereal filtrate from the preparation of auric dibenzyl sulphide dichloride contains dibenzylsulphine oxide, $O:S(C_7H_7)_2$, melting at 133°. The action of hydrogen chloride on a mixture of this and aurodibenzylsulphine chloride in chloroform solution leads to the formation of auric dibenzyl sulphide dichloride. The mechanism of the reactions by which these substances are formed is discussed. G. Y.

Action of Concentrated Feeble Acids on Metallic Chlorides. ALFRED BENRATH (*J. pr. Chem.*, 1905, [ii], 72, 228—237. Compare this vol., ii, 705).—The product obtained by treating a metallic chloride with a concentrated feeble acid is usually a double salt.

Ferric chloride formate, $Fe_2Cl_2(CHO_2)_4,H_2O$, crystallises from a solution of ferric chloride in warm formic acid, on cooling, in small, canary-yellow crystals; it dissolves in warm alcohol, glacial acetic acid, or water to form reddish-brown solutions, and when boiled with water yields a reddish-brown, basic salt. When heated at 110°, it is converted into a brownish-red powder, $Fe_2Cl_6,14Fe_2O_3,18H_2O$, which dissolves in hot hydrochloric acid and forms sodium chloride with boiling aqueous sodium hydroxide.

Ferric chloride acetate, $3Fe_2Cl_2(C_2H_3O_2)_4,C_2H_4O_2,2H_2O$, formed by dissolving ferric chloride in glacial acetic açid, crystallises in small, red rhombohedra, when heated melts and evolves hydrogen chloride, and is easily soluble in water, alcohol, or ether.

Ferric chloride chloroacetate, $Fe_2Cl_2(C_2H_2O_2Cl)_4,H_2O$, formed by fusing ferric chloride with chloroacetic acid, separates, on cooling, in crystals, and decomposes at 100°.

Ferric chloride propionate, $Fe_2Cl_2(C_3H_5O_2)_4$, crystallises from a mixture of ferric chloride and propionic acid in ruby-red crystals. If ferric chloride is boiled in an excess of propionic acid in a reflux condenser, it is reduced partly to ferrous chloride.

Aluminium chloride formate, $Al_2Cl_2(CHO_2)_4,2CH_2O_2,5H_2O$, formed when aluminium chloride is dissolved in formic acid at 60°, separates as a loose, white, deliquescent powder, which has a strong acid reaction. *Aluminium chloride acetate*,

$$2Al_2Cl_2(C_2H_3O_2)_4,Al_2Cl_4(C_2H_3O_2)_2,15H_2O,$$

formed by the action of glacial acetic acid on powdered aluminium chloride or by boiling crystalline aluminium chloride with glacial acetic acid, forms a loose, white, hygroscopic powder, and dissolves in alcohol or water to form solutions with a strongly acid reaction. *Aluminium chloride propionate*, $Al_2Cl_2(C_3H_5O_2)_4$, formed by boiling powdered, sublimed aluminium chloride with an excess of propionic acid, is deliquescent, and when exposed to moist air has a strong odour of propionic acid.

Calcium chloride and formic acid form a syrupy mass which, on treatment with a mixture of ether and alcohol, yields calcium chloride, $CaCl_2,4H_2O$. *Calcium chloride acetate*, $CaCl(C_2H_3O_2),2H_2O$, crystallises on cooling from a solution of calcium chloride in hot glacial

acetic acid; it forms a white, hygroscopic, crystalline powder. On addition of ether to the mother liquor from the double salt, crystalline calcium chloride, $CaCl_2,2H_2O$, or, after some days, $CaCl_2,4H_2O$, is precipitated.

Calcium chloride propionate, $CaCl(C_3H_5O_2),CaCl_2,2C_3H_6O_2,4H_2O$, crystallises from the solution of calcium chloride in propionic acid in long, thin, glistening needles; if ether is added to the solution in calcium chloride, $CaCl_2,2H_2O$, which gradually changes into $CaCl_2,4H_2O$, is precipitated. Strontium chloride, $SrCl_2,2H_2O$, crystallises from the solution of the hexahydrate in glacial acetic acid. Anhydrous stannous chloride crystallises in needles from a solution of the dihydrate in glacial acetic acid, whilst stannic chloride dissolves in glacial acetic acid to form a colourless, non-crystallisable syrup. Some chlorides, for example, mercuric or sodium chloride, can be recrystallised from glacial acetic acid unchanged. G. Y.

Aliphatic Iodochlorides and Iodosochlorides. JOHANNES THIELE and W. PETER (*Ber.*, 1905, 38, 2842—2846).—*Chloroiodofumaric acid*, $C_4H_2O_4ClI$, formed by boiling acetylenedicarboxylic acid with iodine chloride in ethereal solution, crystallises in yellow needles, becomes brown at 180°, sinters at 200°, melts and decomposes at 226—227°, and is easily soluble in water. When treated with chlorine in ice-cooled aqueous solution, this forms the *iodosochloride*, $\begin{array}{l}\mathrm{CCl{\cdot}CO} \\ \|\ \\ \mathrm{CO_2H{\cdot}C{-}ICl}\end{array}\!\!>\!O$, which is obtained as a yellow, crystalline powder, sinters at 116°, melts and decomposes at 119—120°, yields free iodine when treated with potassium iodide, and is reduced by sulphurous acid to chloroiodofumaric acid. When treated with ice-cold alcohol, it is converted into the *iodosochloride* of chloroacrylic acid, $\begin{array}{l}\mathrm{CCl{\cdot}CO} \\ \| \\ \mathrm{CH{\cdot}ICl}\end{array}\!\!>\!O$; this crystallises in matted needles which become red on exposure to light, sinters and melts at 146—147°, liberates iodine from potassium iodide, and on treatment with alcohol at the laboratory temperature yields *α-chloro-β-iodoacrylic acid*, $CHI{:}CCl{\cdot}CO_2H$. This crystallises in yellow leaflets, melts at 88—89°, and is therefore not identical with Stolz's acid (Abstr., 1886, 530). *Chloroiodosoacrylic acid*,

$$\begin{array}{l}\mathrm{CCl{-\!\!-}CO} \\ \| \\ \mathrm{CH{\cdot}I(OH)}\end{array}\!\!>\!O,$$

is formed by the action of boiling water on the iodosochloride of chlorofumaric acid; it crystallises in glistening, colourless prisms, becomes yellow at 150°, softens at 173°, decomposes at 183°, and is reduced by sulphurous acid to chloroiodoacrylic acid. The *acetyl* derivative of iodosochloroacrylic acid, C_3HO_3ClIAc, formed by heating the iodosochloride of chlorofumaric acid with acetic anhydride, crystallises in glistening, yellow needles, sinters at 131°, melts at 138—139°, and when treated with water yields chloroiodosoacrylic acid. Chloroiodoacrylic acid is formed when chlorofumaric iodosochloride is heated with glacial acetic acid on the water-bath.

Methyl iodochloride, $Me{\cdot}ICl_2$, is formed as a heavy, yellow precipitate when methyl iodide is added to a solution of chlorine in a

mixture of carbon tetrachloride and light petroleum cooled by a carbon dioxide-ether mixture. It melts at $-28°$, is decomposed by water with formation of methyl chloride and iodine chloride, and forms methyl iodide and free iodine with a mixture of hydriodic and hydrochloric acids at $-60°$, but methyl chloride at the laboratory temperature.

In the same manner, ethyl, *n*-propyl, and *n*-butyl iodides form *iodochlorides*, which are more soluble in light petroleum, and decompose with formation of iodine chlorides at lower temperatures than methyl iodochloride. *sec.-Butyl iodochloride* is formed in liquid air and decomposes at $-100°$, below which temperature chlorine liberates iodine from *tert.*-butyl iodide; allyl iodide forms an unstable *iodochloride*. *Methylene di-iodochloride* is more stable, being capable of existence for a short space of time when formed by the action of chlorine on the di-iodide in carbon tetrachloride at 0°.

With bromine in light petroleum at the laboratory temperature, iodobenzene forms an *oil* which solidifies when cooled by a mixture of carbon dioxide and ether. The action of bromine on methyl iodide in cooled light petroleum solution leads to the formation of a *substance* which crystallises in large, orange leaflets, decomposes at higher temperatures, and is probably methyl iodobromide. G. Y.

New Acids of the Oleic Series. III. Derivatives of Δ^{α}-Oleic Acid. GIACOMO PONZIO (*Atti R. Accad. Sci. Torino*, 1905, **40**, 970—973. Compare Abstr., 1904, i, 548, and this vol., i, 405).—*β-Bromostearic acid*, $CH_3\cdot[CH_2]_{14}\cdot CHBr\cdot CH_2\cdot CO_2H$, prepared by the action of hydrobromic acid on 2 : 3-oleic acid, crystallises from light petroleum in white plates melting at 54°, and is soluble in all the ordinary organic solvents.

β-Hydroxystearic acid, $CH_3\cdot[CH_2]_{14}\cdot CH(OH)\cdot CH_2\cdot CO_2H$, obtained by the action of alcoholic potassium hydroxide solution on β-bromostearic acid, crystallises from chloroform in white plates melting at 89°, and is soluble in alcohol or ether and to a slight extent in light petroleum. Its *sodium* salt crystallises from alcohol in white prisms. The acid described previously as β-hydroxystearic acid, obtained by Fremy (*Ann. Chim. Phys.*, 1837, [ii], **65**, 113) and by Saytzeff (Abstr., 1887, 30), must have the hydroxyl group elsewhere than the β-position.

αβ-Dihydroxystearic acid, $CH_3\cdot[CH_2]_{14}\cdot CH(OH)\cdot CH(OH)\cdot CO_2H$, prepared by oxidising Δ^{α}-oleic acid with alkaline permanganate solution, crystallises from ethyl acetate in prisms melting at 126°, and is soluble in most organic solvents and slightly so in water. The acid described by Saytzeff as αβ-dihydroxystearic acid (Abstr., 1888, 815) must have another constitution. T. H. P.

Action of Ethyl Sodiomalonate on Ethyl Ethoxysuccinate and Ethyl Ethoxybenzylmalonate. HERMANN STAUDINGER (*Annalen*, 1905, **341**, 99—117).—An attempt has been made to throw further light on the mechanism of condensations of ethyl sodiomalonate with other esters, more especially to ascertain if additive intermediate products are formed.

Ethyl malonate interacts with ethyl fumarate in alcoholic solution in the presence of 1/10 equivalent of sodium, the formation of the additive product taking place rapidly with development of heat. Ethyl ethoxysuccinate combines with ethyl malonate in the presence of one equivalent of sodium, but heat is not developed; if 1/10 equivalent of sodium is used, a very small amount of condensation takes place. In benzene solution, the addition of ethyl malonate to ethyl fumarate is complete, but there is no reaction with ethyl ethoxysuccinate. This fact demonstrates that the reaction does not depend on the formation of an additive product of sodium ethoxide with one of the reagents, for example, the ethyl malonate. Probably the ethyl sodiomalonate unites directly at the ethylene linking.

Ethyl benzylidenemalonate and ethyl ethoxybenzylmalonate were similarly compared with respect to their behaviour towards ethyl malonate in the presence of sodium ethoxide. The results obtained confirmed in every way the conclusions arrived at in the case of ethyl fumarate and ethyl ethoxysuccinate. K. J. P. O.

Ethylmalic Acid. OSCAR DOEBNER and L. SEGELITZ (*Ber.*, 1905, **38**, 2733—2737).—*γ-Trichloro-β-hydroxy-α-ethylbutyric acid*,

$$CCl_3\cdot CH(OH)\cdot CHEt\cdot CO_2H,$$

prepared by the condensation of ethylmalonic acid with chloral by means of pyridine, separates from chloroform in glistening needles and melts at 137°. The *silver*, *barium*, *calcium*, and *copper* salts were prepared. The *methyl ester* separates from methyl alcohol in stellate crystals and melts at 76°.

When γ-trichloro-β-hydroxy-α-ethylbutyric acid is warmed with a 10 per cent. aqueous solution of potassium hydroxide, potassium β-ethylmalate is formed, thus: $CCl_3\cdot CH(OH)\cdot CHEt\cdot CO_2H + 5KOH = 3KCl + 3H_2O + CO_2K\cdot CH(OH)\cdot CHEt\cdot CO_2K$. *β-Ethylmalic acid* crystallises with difficulty but is not so hygroscopic as malic acid; it melts and decomposes at 86—87°. Its *silver*, *lead*, *copper*, and *zinc* salts are described. When β-ethylmalic acid is heated at about 200°, ethylmaleic acid is formed. A. McK.

Constitution of Meta-saccharinic Acid. HEINRICH KILIANI and PETER LOEFFLER (*Ber.*, 1905, **38**, 2667—2670. Compare Kiliani and Naegell, Abstr., 1903, i, 10).—A 36 per cent. yield of pure meta-saccharopentose is obtained by distilling barium meta-saccharinate. The *phenylbenzylhydrazone*, $C_5H_{10}O_3,C_{13}H_{12}N_2$, crystallises in yellow, prismatic needles and melts at 117—118°.

On reduction with red phosphorus and concentrated hydriodic acid in a sealed tube at 140° for 7 hours, βγδ-trihydroxyvaleric acid, formed by the action of bromine on meta-saccharopentose, yields *n*-valerolactone and a small quantity of an unsaturated *acid*, $C_5H_8O_3$, which forms a *calcium* salt, $Ca(C_5H_7O_3)_2,2H_2O$, crystallising in stout prisms.

Meta-saccharinic acid has therefore the methylene group in the β-position and meta-saccharopentose has the constitution

$$OH\cdot CH_2\cdot [CH\cdot OH]_2\cdot CH_2\cdot CHO,$$

and the trihydroxyvaleric acid, $OH\cdot CH_2\cdot [CH\cdot OH]_2\cdot CH_2\cdot CO_2H$.

G. Y.

The Active Components of Fehling's Solution. FRANCIS MARRE and STOLLE (*Chem. Centr.*, 1905, ii, 615; from *Rev. gén. Chim. pure appl.*, [vii], 8, 256—258. Compare Bullnheimer and Seitz, Abstr., 1899, i, 888; 1900, i, 330).—If in preparing Fehling's solution the copper sulphate is replaced by the calculated amount of copper hydroxide and the salts dissolved in as little warm water as possible, there separates out the substance $C_8H_4O_{12}CuNa_4K_2,H_2O$, which is the active component of Fehling's solution. It may have the constitution $Cu[O\cdot CH(CO_2Na)\cdot CH(OK)\cdot CO_2Na]_2$ or

$$Cu[O\cdot CH(CO_2Na)\cdot CH(ONa)\cdot CO_2K]_2.$$

G. Y.

Symmetrical Dialkyl Esters of Citric Acid. GEORG SCHROETER (*Ber.*, 1905, 38, 3190—3201. Compare Schroeter and Schmitz, Abstr., 1902, i, 531).—[With LEONHARD SCHMITZ.]—*Methyl dihydrogen citrate*, $CO_2H\cdot CH_2\cdot C(OH)(CO_2H)\cdot CH_2\cdot CO_2Me$, is obtained from the mother liquors from the preparation of *s*-dimethyl hydrogen citrate (*loc. cit.*); it crystallises from glacial acetic acid or acetone and melts at 166—167°.

s-Dimethyl hydrogen acetylcitrate, $OAc\cdot C(CH_2\cdot CO_2Me)_2\cdot CO_2H$, formed by the action of acetic anhydride and concentrated sulphuric acid on the dimethyl ester, separates from a mixture of chloroform and light petroleum in nodular crystals, melts at 75°, and is easily soluble in water, alcohol, ether, chloroform, or ethyl acetate. When boiled with absolute methyl alcohol, acetylcitric anhydride forms *methyl dihydrogen acetylcitrate*, $CO_2Me\cdot CH_2\cdot C(OAc)(CO_2H)\cdot CH_2\cdot CO_2H$, which is obtained as a syrup, and is converted by boiling acetyl chloride into the *methyl* ester of acetylcitric anhydride,

$$\begin{array}{l}CO_2Me\cdot CH_2\cdot C(OAc)\cdot CO \\ \qquad\qquad\quad\; | \\ \qquad\qquad\quad CH_2\text{——}CO\end{array}\!\!>O\,;$$

this crystallises in white needles, melts at 108—110°, and when warmed with methyl alcohol yields *s*-dimethyl hydrogen acetylcitrate, which reacts with phosphorus pentachloride to form the *chloride*, $OAc\cdot C(CH_2\cdot CO_2Me)_2\cdot COCl$, as a yellow oil. Owing to its instability towards moisture and heat, this could not be obtained in a state of purity; when treated with anhydrous ammonia in chloroform solution, it forms the *amide*, $OAc\cdot C(CH_2\cdot CO_2Me)_2\cdot CO\cdot NH_2$, which separates from a mixture of chloroform and ether in prismatic crystals, melts at 108—109°, and is easily soluble in water and most organic solvents, but is only sparingly so in ether or light petroleum.

[With R. SCHWAMBORN.]—When warmed with sulphuric acid, *s*-dimethyl hydrogen citrate decomposes with evolution of carbon monoxide and formation of acetonedicarboxylic acid.

[With LEONHARD SCHMITZ.]—The *nitrile*, $CN\cdot C(OH)(CH_2\cdot CO_2Me)_2$, is formed when the calculated amount of fuming hydrochloric acid is added to a mixture of potassium cyanide and dimethyl acetonedicarboxylate in ethereal solution; it crystallises from water or chloroform, melts at 53°, and when dissolved in cold concentrated sulphuric acid is hydrolysed to the *amide*, $NH_2\cdot CO\cdot C(OH)(CH_2\cdot CO_2Me)_2$, which crystallises from a mixture of chloroform and light petroleum and melts at 106—107°. This dissolves without change in cold concentrated sulphuric acid or in acetic anhydride, but is converted by

acetyl chloride into a *substance* which has C = 47·21, H = 5·78, N = 5·03 per cent., crystallises from hot water, and melts at 103—104°. When carefully treated with the calculated amount of sodium nitrite in strongly cooled concentrated sulphuric acid solution, the amide is converted into *s*-dimethyl hydrogen citrate melting at 125—126°.

[With R. SCHWAMBORN.]—*s-Diethyl hydrogen citrate*,

$$OH\cdot C(CH_2\cdot CO_2Et)_2\cdot CO_2H,$$

is prepared by boiling citric acid with absolute alcohol and a small amount of concentrated sulphuric acid; the ester is isolated as the calcium salt; it is an oil which is easily soluble in water, and can be extracted from its aqueous solution by means of ether. The *silver* salt, $C_{10}H_{15}O_7Ag$, crystallised in voluminous, slender leaflets. The *amide*, $OH\cdot C(CH_2\cdot CO_2Et)_2\cdot CO\cdot NH_2$, can be prepared by the action of potassium cyanide and hydrochloric acid on ethyl acetonedicarboxylate and hydrolysis of the *nitrile* so obtained by means of cold concentrated sulphuric acid; it crystallises from a mixture of chloroform and light petroleum in slender, white needles, and sinters and melts at 74°. On hydrolysis with aqueous sodium hydroxide, it yields *citramonamic acid*, $OH\cdot C(CH_2\cdot CO_2H)_2\cdot CO\cdot NH_2$, which forms a *silver* salt, $C_6H_7O_6NAg_2$, crystallising in slender, white needles, and is not identical with Behrmann and Hofmann's acid (Abstr., 1885, 138), which is probably

$$OH\cdot C(CH_2\cdot CO_2H)(CO_2H)\cdot CH_2\cdot CO\cdot NH_2.$$

When distilled under 13 mm. pressure, the ester-amide yields alcohol and a *substance* which distils at 180—230°, and, on hydrolysis with aqueous sodium hydroxide, forms the *imide*,

$$\begin{array}{l} CO_2H\cdot CH_2\cdot C(OH)\cdot CO \\ \qquad\qquad\quad | \\ \qquad\qquad\quad CH_2\text{—}CO \end{array}\!\!>\!NH;$$

this forms a *silver* salt, $C_6H_6O_5NAg,AgNO_3$. When heated with phenylcarbimide in benzene solution, the ester-amide forms the *phenylurethane*, $NHPh\cdot CO\cdot O\cdot C(CH_2\cdot CO_2Et)_2\cdot CO\cdot NH_2$, which crystallises from alcohol and melts and decomposes at 146°.

The ester-amide interacts with benzoyl chloride at 130° to form the *benzoyl* derivative, $\begin{array}{l} OBz\cdot C(CH_2\cdot CO_2Et)\cdot CO \\ \quad\;\; | \\ \quad\;\; CH_2\text{————}CO \end{array}\!\!>\!NH$, which crystallises in needles, melts at 115°, and when treated with 2*N*-sodium hydroxide forms a blood-red solution which rapidly becomes colourless and, on addition of the calculated quantity of hydrochloric acid, yields benzoic acid, and, on a further addition of hydrochloric acid and cooling to 0°, the *as*-imide of aconitic acid melting at 191° (this vol., i, 819).

G. Y.

Dihydroxypropanetricarboxylic and αγ-Dihydroxyglutaric Acids. HEINRICH KILIANI and F. HEROLD (*Ber.*, 1905, 38, 2671—2676. Compare Kiliani, Abstr., 1885, 744; 1886, 48; Ruff and Meusser, Abstr., 1902, i, 591).—αγ-Dihydroxypropane-ααγ-tricarboxylic acid is prepared best by warming calcium *iso*saccharinate with concentrated nitric acid at 35° and finally at 45—50°. After removal of the calcium oxalate, the product is evaporated with sufficient calcium carbonate to form the normal salt, which is dissolved in water

and converted into the acid salt by precipitation of two-thirds of the calcium with oxalic acid. The filtrate, after concentration, slowly deposits the acid calcium salt of the lactone, $(C_6H_5O_7)_2Ca,2H_2O$ or $5H_2O$, which crystallises in thin prisms, and loses water and commences to decompose at 100—120°. The tricarboxylic acid is obtained, on evaporation of its solution in a vacuum, as a viscid syrup, which crystallises in deliquescent plates and prisms. The *copper* salt, $(C_6H_5O_8)_2Cu_3$, is light blue; the *quinine* salt, $C_6H_8O_8,3C_{20}H_{24}O_2N_2,3H_2O$, crystallises in sheaves of needles and melts at 142°.

$\alpha\gamma$-Dihydroxyglutaric acid is obtained in the form of its *lactone*, $(C_5H_6O_5)_2,H_2O$, which melts at 164—165°, by boiling the acid calcium salt just mentioned with the calculated amount of aqueous oxalic acid, evaporating the filtrate in a vacuum, and washing the crystalline residue with a small amount of water.

$\alpha\gamma$-Dihydroxyglutaric acid, free from its lactone, is obtained by treating its calcium salt with oxalic acid and evaporating the filtrate over sulphuric acid in a vacuum; it crystallises in colourless plates or prisms, commences to soften at 115°, and melts above 120°. The *zinc*, $2C_5H_6O_6Zn,3H_2O$, and the *copper*, $C_5H_6O_6Cu,H_2O$, salts are described.

G. Y.

Formation of Complex Salts with Thio-acids. II. Thiolmalic Acids and their Salts. ARTHUR ROSENHEIM and WILHELM STADLER (*Ber.*, 1905, **38**, 2687—2690. Compare Rosenheim and Davidsohn, Abstr., 1904, i, 843; Biilmann, this vol., i, 625).—Thiolmalic acid melts at 150° and has the molecular conductivity $\mu = 46{\cdot}0$ with $v = 32$ or $\mu = 251{\cdot}2$ with $v = 2048$ at 25°, and the affinity constant $K = 0{\cdot}0523$. It forms an alcoholic or aqueous solution, neutral to phenolphthalein, on addition of 2 mols. of sodium hydroxide, and for oxidation requires about five equivalents of iodine, as also more potassium permanganate than is necessary for its conversion into dithiodimalic acid. The *ethyl* ester, $CO_2Et{\cdot}CH(SH){\cdot}CH_2{\cdot}CO_2Et$, is an oil which boils with partial decomposition at 246°; the *benzyl* ester boils and decomposes at 250—280°. The *mono-sodium*, $C_4H_5O_4SNa,\frac{1}{2}H_2O$, and *mono-ammonium* salts are crystalline; the *di-alkali* salts form vitreous masses; the crystalline *di-barium*, $C_4H_4O_4SBa,\frac{1}{2}H_2O$, and di-zinc salts are described; the *tri-alkali thiolmalates* form amorphous, flocculent precipitates. Sodium thiolmalate in neutral aqueous solution gives with cobalt carbonate a brownish-red, with bismuth carbonate a yellow, coloration. On dissolving zinc carbonate in aqueous dipotassium thiolmalate and evaporating the solution, an amorphous, hygroscopic mass is obtained; with barium chloride in aqueous solution, this forms a complex *barium zinc* salt,

$$Ba_3Zn_2(OH)(C_4H_3O_4S)_3,5H_2O,$$

which is obtained as a flocculent, white precipitate. G. Y.

Formaldehyde and Formate Formation. FRIEDRICH AUERBACH (*Ber.*, 1905, **38**, 2833—2836).—A criticism of Euler and Euler's paper (this vol., i, 633). G. Y.

Action of Acetaldehyde and Acetone on Mercuric Acetate. A. LASSERRE (*J. Pharm. Chim.*, 1905, [vi], **22**, 246—249).—A cold

aqueous solution of mercuric acetate is reduced by the action of aliphatic aldehydes, paraldehyde, acetals, or aldoses, mercurous acetate crystallising from the solution after some hours. The aliphatic alcohols, acetone, or the ketoses have no such reducing action. The *compound* CMeHO,HgO, obtained by the addition of sodium hydroxide to a solution of mercuric acetate and acetaldehyde at 0°, is a pale yellow powder, deflagrating at 180°, soluble in solutions of mercuric acetate, potassium iodide, sodium thiosulphate, or hydrogen sulphite, and insoluble in water, sulphuric, acetic, tartaric, or oxalic acid or in the ordinary organic solvents (compare Leys, this vol., ii, 655). The *compound* $COMe_2,2HgO$, obtained by warming an alkaline solution of mercuric acetate and acetone, is a yellow powder, insoluble in water and yielding acetone on distillation with dilute phosphoric acid; the *compound* $(COMeEt)_2,3HgO$ is similarly obtained from methyl ethyl ketone (compare Reynolds, Abstr., 1871, 561). M. A. W.

Action of Bases on Chloral Hydrate. JOHANNES E. ENKLAAR (*Rec. Trav. chim.*, 1905, [ii], **24**, 419—444. Compare Werner, Trans., 1904, **85**, 1376, and Böttger and Kötz, Abstr., 1902, i, 659).—The results of further experiments on the velocity of decomposition of chloral hydrate by calcium hydroxide in the presence of neutral salts serve to show that the second explanation of the mechanism of the reaction already suggested by the author (compare this vol., i, 170) is the correct one, namely, the salt of chloral hydrate which is first formed is highly dissociated in solution, and the complex negative ion breaks down into chloroform and the negative ion of formic acid, according to the equations $CCl_3\cdot CH(OH)_2 + KOH \rightleftarrows CCl_3\cdot CH(OH)\cdot OK + H_2O$; $CCl_3\cdot CH(OH)\cdot OK \rightleftarrows CCl_3\cdot CH(OH)\cdot O^- + \overset{+}{K}$; $CCl_3\cdot CH(OH)\cdot O^- = CHCl_3 + CHO\cdot O^-$. That chloral hydrate is a feeble acid and therefore capable of forming salts is shown by the fact that it has a specific conductivity of $6{\cdot}57$ to $5{\cdot}73 \times 10^{-6}$ in $N/100$ solution at 0·65°, the corresponding values for calcium formate and calcium hydroxide being $522{\cdot}9 \times 10^{-6}$ and 1372×10^{-6} respectively, the conductivity of water being $2{\cdot}5$ to $2{\cdot}4 \times 10^{-6}$. M. A. W.

Transformations of the Isomeric Trithioaldehydes. J. F. SUYVER (*Rec. Trav. chim.*, 1905, [ii], **24**, 377—403. Compare Baumann and Fromm, Abstr., 1891, 1010).—α-Trithioaldehyde (m. p. 100—101°) is not transformed into the β-isomeride (m. p. 125—126°) by the action of heat, for it is unchanged after heating at 140° for 24 hours, but certain catalytic agents, such as hydrogen chloride, iodine, zinc chloride, acetyl chloride, ethyl iodide, Beckmann's mixture, or sulphur trioxide or sulphonyl chloride dissolved in chloroform, acting on the substance either fused or in solution, convert it into the β-isomeride to the extent of from 89 to 98 per cent., and the reaction is a balanced one, for β-trithioaldehyde is transformed into the α-isomeride to the extent of from 11 to 2 per cent. under similar conditions. It was not possible to separate the two isomerides in the equilibrium mixtures by the action of solvents, as the solubility of each compound in the ordinary organic solvents is the same; the composition of the mixtures

was therefore determined by comparing their solidifying points with those of mixtures containing known proportions of the two isomerides. α-Trithiobenzaldehyde (m. p. 166—167°) is converted into the β-isomeride (m. p. 225—226°) to a small extent on heating, to the extent of 2·9 per cent. on boiling in benzene solution at 81°, or to 17·4 per cent. in toluene at 111°; such catalytic agents as acetyl chloride, hydrogen chloride in alcoholic solution, or sulphur trioxide or iodine in chloroform solution completely convert the α-compound into the β-isomeride; whilst Beckmann's mixture, or a solution of iodine in carbon bisulphide, toluene, or benzene, effects a partial conversion. The transformation of α-trithiobenzaldehyde into the β-isomeride is not a reversible reaction, and the relative proportion of the two isomerides in the final mixtures is determined by extraction with benzene, in which solvent the α-isomeride is soluble to the extent of 6·08 parts in 100 parts of solvent at 25°, whilst the β-isomeride is practically insoluble. M. A. W.

Ketone and Aldehyde Reactions. Pavel Iw. Petrenko-Kritschenko [with Eugen Eltschaninoff, E. Kestner and Th. Dolgopoloff] (*Annalen*, 1905, **341**, 150—171).—The velocity of the reaction of various aliphatic, aromatic, and cyclic saturated ketones and aldehydes with phenylhydrazine and potassium hydrogen sulphite has been measured. The results have been previously published (Abstr., 1903, i, 440, and this vol., i, 354). K. J. P. O.

Compounds of Ketones and Aldehydes with Mercuric Oxide. S. M. Auld and Arthur Hantzsch (*Ber.*, 1905, **38**, 2677—2685).—Trimercuridiacetone hydroxide,

$$O\Big<\begin{matrix}CMe(OH)\cdot CH(Hg\cdot OH)\\ CMe(OH)\cdot CH(Hg\cdot OH)\end{matrix}\Big>Hg,$$

is formed by the action of freshly precipitated mercuric oxide on acetone in aqueous solution in presence of baryta (compare Reynolds, this Journal, 1871, **24**, 561). The baryta is precipitated by means of carbon dioxide, the excess of the latter removed by a current of air, and the filtrate evaporated, when the product is obtained as a sticky syrup, which dissolves in much water, forming a clear, almost colourless solution. This has a slight alkaline reaction and the electrical conductivity $\mu = 0·018$ with $v = 256$ or $\mu = 0·022$ with $v = 512$ at 18°. The haloid salts are formed by carefully adding hydrogen haloids to the aqueous solution of the hydroxide. The *dichloride*, $C_6H_{10}O_3Hg_3Cl_2$, forms a colourless powder, which becomes yellow when heated, melts at about 110°, is easily soluble in pyridine or aniline, but only sparingly so in alcohol, and is almost insoluble in water; the *platinichloride*, $C_6H_{10}O_3Hg_3,PtCl_6$, forms an amorphous, brown precipitate and detonates at 178°; the *dibromide* crystallises in small, white needles and melts at 127°; the *di-iodide*, formed by the action of cold acetic acid on a mixture of the hydroxide and potassium iodide, crystallises in small needles and melts at 104°; the *picrate*,

$$2C_6H_{12}O_5Hg_3,C_6H_3O_7N_3,6H_2O,$$

forms small, yellow crystals, is easily soluble in hot water, and has the

electrical conductivity $\mu = 0{\cdot}042$ with $v = 1100$ at 25°. On adding concentrated hydrogen haloids or strong oxy-acids to the hydroxide, immediate decomposition to acetone and the mercuric salt takes place, but if a slight excess of hydrochloric acid having $v = 40$ is added to a solution of the base with $v = 512$, the reaction takes place more slowly, and the solution has the electrical conductivities $\mu = 0{\cdot}00213$, 0·00214, 0·00200, 0·00195, 0·00191, and 0·00187 respectively 1, 3, 6, 8, 12, and 25 minutes after mixing.

The action of bromine in potassium bromide solution on the aqueous solution of the base leads to the formation of mercuric dibromide and *as*-dibromoacetone, which, on prolonged shaking of the mixture, is converted into methylglyoxime.

Reynolds' insoluble polymeride of trimercuridiacetone hydroxide (*loc. cit.*) is formed by the action of alkali hydroxides or, more slowly, of salts or of sunlight on the aqueous solution of the base. The action of boiling aqueous alkali hydroxides on the base or its polymeride leads to the formation of acetone and acetonemercarbide,

$$COMe{\cdot}C(\vdots Hg_2O){\cdot}Hg{\cdot}OH,$$

which is identical with Hofmann's compound (Abstr., 1898, i, 635). Acetophenone and mercuric oxide interact only on prolonged digestion at 100° to form a yellow, insoluble *product* which, on treatment with hydrochloric acid, yields acetophenone and mercuric chloride.

The action of mercuric oxide on acetaldehyde in slightly alkaline solution leads to the formation of a colourless solution which probably contains trimercuridialdehyde hydroxide, as it is indifferent towards phenylhydrazine, hydroxylamine, or rosaniline decolorised by sulphurous acid. The base cannot be isolated, as it changes more easily than the acetone compound into the *polymeride*, $(C_4H_8O_5Hg_3)_x$, which is formed immediately as a white powder by warming a dilute solution of acetaldehyde with a solution of mercuric chloride made alkaline with potassium hydroxide. This may be used as a test to detect the presence of small quantities of acetaldehyde (1 in 6000 aq.). The polymeride decomposes without melting at about 100°, is practically insoluble in all organic solvents, and is decomposed by hydrochloric acid, but not by dilute acetic acid, with formation of acetaldehyde and mercuric chloride. G. Y.

Complex Compounds of α-Dioximes. Leo Tschugaeff (*Zeit. anorg. Chem.*, 1905, **46**, 144—169).—The α-dioximes differ from all others in reacting with nickel, cobalt, iron, platinum, palladium, and copper salts to form stable salts, called by the author *dioximines.*

The nickel derivative of dimethylglyoxime, *nickel dimethylglyoximine*, $\left(\begin{matrix}CMe{:}NO\\ |\\ CMe{:}NO\end{matrix}\right)Ni\left(\begin{matrix}CMe{:}NOH\\ |\\ CMe{:}NOH\end{matrix}\right)$, is obtained as a scarlet, crystalline precipitate on adding a hot saturated alcoholic solution of dimethylglyoxime to one of nickel acetate. It is almost insoluble in water, slightly soluble in alcohol, ether, benzene, glacial acetic acid, or pyridine. It can be sublimed undecomposed and is very stable towards most reagents. Alkali hydroxides and ammonia, alkali and ammonium carbonates, and hydrogen sulphide do not attack it; ammonium

sulphide acts only slowly. Weak acids have no action, but with strong acids the reversible reaction, $C_8H_{14}O_4N_4Ni + 2HX \rightleftharpoons 2C_4H_8O_2N_2 + NiX_2$, takes place. The remaining glyoximines described closely resemble the nickel compound.

Nickel methylethylglyoximine, $C_{10}H_{18}O_4N_4Ni$, forms brownish-red, prismatic crystals and melts at about 280°. *Nickel methylpropylglyoximine*, $C_{12}H_{22}O_4N_4Ni$, is obtained by digesting nickel acetate with the oxime in aqueous alcoholic solution. It forms orange-red crystals and melts at about 144°. It is even more soluble than the preceding compounds in organic solvents; the solution in benzene shows a freezing point corresponding with the above molecular weight. *Nickel methyl*iso*butylglyoximine*, $C_{14}H_{26}O_4N_4Ni$, forms orange-red needles and melts at 160°. *Nickel diphenylglyoximine*, $C_{24}H_{22}O_4N_4Ni$, formed from nickel acetate and α-benzildioxime, melts and decomposes at 300°. *Nickel ditolylglyoximine*, $C_{32}H_{30}O_4N_4Ni$, is somewhat more soluble than diphenylglyoximine in organic solvents; it forms brownish-red prisms. *Nickel carbethoxylmethylglyoximine*, $C_{12}H_{18}O_8N_4Ni$, forms dark brownish-violet needles, melts at 202·5—203·5°, is fairly soluble in organic solvents, and sublimes when heated in a vacuum. It is more easily attacked by reagents than the remaining glyoximines.

The platinoglyoximines are all crystalline, closely resemble the nickel glyoximines, and are formed by adding a boiling acetic acid solution of the glyoxime to a boiling aqueous solution of potassium platinochloride or platinum-*cis*-dichlorodipyridine, and after addition of ammonium acetate digesting for a time on the water-bath. The platinodioximines are even more stable than the nickel compounds; as in the case of the latter, potassium cyanide appears to be the only reagent which easily and completely decomposes them with separation of free dioxime. They are soluble in dilute alkalis and take up bromine to form dibromides. In a vacuum they can be sublimed without decomposition.

Platinomethylethylglyoximine, $C_{10}H_{18}O_4N_4Pt$, forms dark brown needles. *Platinimethylethylglyoximine bromide*, $C_{10}H_{18}O_4N_4PtBr_2$, is formed when bromine is added to the preceding compound in chloroform solution. It separates as a brown, crystalline powder, moderately soluble in most organic solvents, very slightly soluble in water. It is very stable towards acids, but is reduced by hydrogen sulphide. *Platinomethylpropylglyoximine*, $C_{12}H_{22}O_4N_4Pt$, has a normal molecular weight in benzene solution, and forms brown needles which melt at 252°.

*Platinomethyl*iso*butylglyoximine*, $C_{14}H_{26}O_4N_4Pt$, melts at about 220°. *Platinodiphenylglyoximine*, $C_{28}H_{22}O_4N_4Pt$, is best obtained by digesting platinum-*cis*-dichlorodipyridine with α-benzildioxime in aqueous acetic acid solution. It forms reddish-brown needles which are decomposed by heating to a high temperature, are only very slightly volatile even in a vacuum, and dissolve very sparingly in organic solvents.

Palladomethylethylglyoximine, $C_{10}H_{18}O_4N_4Pd$, prepared from palladium ammonium chloride and methylethylglyoxime, forms canary-yellow needles which melt and decompose at about 290° but can be sublimed unchanged in a vacuum. *Palladomethylpropylglyoximine*,

$C_{12}H_{22}O_4N_4Pd$, melts at 176—177°. *Palladodiphenylglyoximine*, prepared by adding a concentrated aqueous solution of palladium ammonium chloride to a solution of α-benzildioxime in pyridine, has not been further examined.

Cupric dimethylglyoximine, $C_8H_{14}O_4N_4Cu$, forms dark crystals which are soluble in water and most other solvents to dark brown solutions. It decomposes on heating at 200°, and cannot be sublimed in a vacuum without decomposition. It is less stable towards reagents than the corresponding nickel, platinum, and palladium compounds.

Bivalent iron does not appear to form simple compounds like those given by the preceding four metals. Complex compounds are easily obtained which contain the dioxime group in combination with bases like pyridine. A number of these have been prepared qualitatively from α-dioximes which contain both hydroxyls in the *cis*-position. *Ferrodipyridinemethylglyoximine*, $C_{20}H_{28}O_4N_6Fe$, prepared by the action of a concentrated aqueous solution of ferrous sulphate on an alcoholic solution of methylethylglyoxime to which excess of pyridine has been added, forms brownish-red, dichroic prisms easily soluble in pyridine, more sparingly in alcohol, chloroform, or benzene, scarcely at all in water.

Cobaltous dioximines have not yet been prepared in a pure condition, but strongly basic complex cobaltic dioximines, which contain besides the dioximine group also ammonia or other base, are easily obtained. *Cobaltodiamminedimethylglyoximine chloride*,

$$(C_8H_{14}O_4N_4Co,2NH_3)Cl,5H_2O,$$

is formed by the action of roseopentamminecobaltic chloride or purpureocobaltic chloride on dimethylglyoximine. The electrical conductivity shows that the compound must be grouped with the tetrammine bases of the general formula $(Co,4ClX_2)X'$. It forms yellowish brown crystals easily soluble in hot water, very sparingly soluble in alcohol or ether.

The *base* $(C_8H_{14}O_4N_4Co,2NH_3)OH$ is obtained in solution by the action of silver hydroxide on a concentrated solution of the hydrochloride. It is strongly alkaline. The *nitrate*, $C_8H_{20}O_7N_7Co$, formed by interaction of the hydrochloride and sodium nitrate, crystallises in anhydrous, yellow needles. The *sulphate*, $[C_8H_{20}O_4N_6Co]_2SO_4$, forms thick, microscopic, yellow tablets; according to molecular weight and conductivity experiments, it dissociates into three ions.

A comparison of, for instance, a platinodioximine with Peyrone's salt, $Pt,2NH_3Cl_2$, shows that in the dioximine the two NO groups correspond with the two chlorine atoms, and the two NOH groups with the two ammonia molecules. The two NO groups play the part of a dibasic acid, and the two NOH groups the *rôle* of a diacid base. According to Werner's theory, the NO groups are to be regarded as attached to the platinum by major, the NOH groups by minor, valencies: $\begin{matrix}:NO \\ :NO\end{matrix}\!\!>\!Pt\!<\!\!\begin{matrix}\cdot NOH: \\ \cdot NOH:\end{matrix}$. Similar expressions may be used for the dioximines of the other metals mentioned above. The dibromide, $C_8H_{18}O_4N_4Br_2Pt$, which appears to be analogous with Gerhardt and Cleve's compounds $(Pt,2NH_3X_4)$, may be deduced in corresponding manner from the quadrivalent platinum atom with the co-ordination number six.

If it is assumed that in the dioximine molecule not only the NO but also the NOH residue is in direct union with the metal, then the assumption must also be made that in these compounds cyclic atomic unions are present. Thus the construction of the dioximines may possibly be expressed by one of the following formulæ:

$$\text{I. } \begin{matrix} R\cdot C{=}NO \\ | \\ R\cdot C{:}NOH \end{matrix} {>}Me{<} \begin{matrix} NO{=}C\cdot R \\ | \\ NOH{:}C\cdot R \end{matrix} \qquad \text{II. } \begin{matrix} R\cdot C{:}NO \\ | \\ R\cdot C{:}NO \end{matrix} {>}Me{<} \begin{matrix} NOH{:}C\cdot R \\ | \\ NOH{:}C\cdot R \end{matrix}$$

The stability of the dioximines is consistent with a cyclic formula.

D. H. J.

Formation of Isodynamic Glucosides with reference to the Theory of Isomeric Change and the Selective Action of Enzymes. Preparation of β-Methylglucoside. E. Frankland Armstrong and S. L. Courtauld (*Proc. Physiol. Soc.*, 1905, iv; *J. Physiol.*, 33).—Use is constantly made of the stereoisomeric glucosides as test materials in studying enzyme action, and it is important to be able to prepare them easily. The following method renders β-methyl glucoside readily obtainable. When solid anhydrous α-glucose is dissolved in dry methyl alcohol containing dry gaseous hydrogen chloride, it is rapidly changed into a mixture of nearly equal parts of α- and β-glucose, which then undergo etherification, yielding a mixture of the two glucosides in nearly equal amounts. If the solution is neutralised before the further slow conversion of the β-methyl glucoside into the more stable α-isomeride can take place, and the solvent is removed, a mixture of the two glucosides is obtained. The α-glucoside is then best destroyed by fermenting it with Hansen's *Saccharomyces intermedians*, and the pure β-compound is left. Of this, 230 grams can be obtained from 500 of dextrose. The α-isomeride is best prepared by Fischer's method, namely, by using less acid and heating until an equilibrated mixture of the two glucosides is obtained; this contains 77 per cent. of the α-compound. After the greater part of this has crystallised out, the mother liquors may again be heated so as to convert part of the β-glucoside into the α-form; this may finally be purified from traces of the β-compound by treatment with emulsin.

W. D. H.

Fucosephenylosazone. W. Mayer and Bernhard Tollens (*Ber.*, 1905, 38, 3021—3022. Compare Müther and Tollens, Abstr., 1904, i, 226).—Pure fucosephenylosazone melts at $177\cdot5^\circ$, and is undoubtedly the antipodal isomeride of rhodeosephenylosazone. It is best prepared by Votoček's method (Abstr., 1904, i, 975), the mixture being heated for $1\frac{1}{4}$ hours. The products of low melting point described previously were mixtures of hydrazone and osazone.

J. J. S.

Cellulose. Hans Riesenfeld and F. Taurke (*Ber.*, 1905, 38, 2798—2800).—A specimen of wood cellulose was insoluble in Schweizer's reagent, but dissolved in an ammoniacal solution of cupric carbonate. Salts, acids, water, or alcohol yielded precipitates with the solution. Metallic zinc, cadmium, aluminium, and lead completely precipitated the cellulose as well as the copper, whereas iron, nickel, and tin were without action.

When heated, the solution produced a brownish-black precipitate, containing about 56 per cent. of copper and 23—26 per cent. of cellulose. J. J. S.

Mutual Solubilities of Diethylamine and Water. ROBERT TABOR LATTEY (*Phil. Mag.*, 1905, [vi], **10**, 397—399. Compare Guthrie, Abstr., 1885, 339).—Diethylamine and water form a pair of liquids which are completely miscible below a certain temperature, above which they become partially miscible. In the following table the temperatures of separation of various mixtures are given:

Per cent. amine	21·73	22·65	25·04	25·06	28·60	30·93	34·03	38·18
Temperature of separation.	154·5°	151·7°	147·5°	147·0°	144·4°	144·0°	143·2°	143·5
Per cent. amine	39·63	45·78	48·89	51·71	54·24	54·78	58·59	58·99
Temperature of separation.	143·5°	144·15°	145·0°	146·8°	148·5°	150·3°	152·3°	156·0°

The critical temperature is 143·5° and the critical concentration of the amine 37·4 per cent., whereas the older experiments of Guthrie give 121° and 19 per cent.

It was found that trustworthy data could only be obtained when the liquids were heated in Jena glass tubes, and the inaccuracy of Guthrie's observations is attributable to the solvent action of the liquid on the glass of the apparatus used. H. M. D.

Constitution of Ammonium Salts. JOHN C. CAIN (*Ber.*, 1905, **38**, 2715—2716).—The author discusses the reactions of dibromides of tertiary amines (compare Hantzsch, this vol., i, 576), the action of hypochlorous acid on trimethylamine, and the action of hydrogen chloride on trimethylamine oxide, from the standpoint of the theory of ammonium salts formerly advanced by him (Abstr., 1904, ii, 726). A. McK.

Supposed Isomerism of Tetramethylammonium Iodide Mercuricyanide. S. M. AULD and ARTHUR HANTZSCH (*Ber.*, 1905, **38**, 2685—2686).—Contrary to the statement of Claus and Merck (Abstr., 1884, 338), only one, the white, tetramethylammonium iodide mercuricyanide is formed by the action of mercuric cyanide on tetramethylammonium iodide in aqueous solution. If these salts are allowed to interact in dilute acetic acid solution and the product boiled with water, hydrogen cyanide is evolved and two salts are formed: the one, $2NMe_4I,3HgI_2,HgI\cdot OH$, crystallises from acetone in large, deep yellow prisms, melts at 187—188°, and is almost insoluble in water. The second, $2NMe_4I,HgI_2,HgI\cdot OH$, forms small, yellow crystals, melts at 246°, is slightly soluble in water, and easily decomposes with formation of mercuric iodide. G. Y.

Aminoethyl Ether. LUDWIG KNORR and GEORG MEYER (*Ber.*, 1905, **38**, 3129—3136. Compare Knorr, Abstr., 1904, i, 854, 916, 938).—Aminoethyl ether has the sp. gr. 0·8512 at 20°/4°, n_D 1·4101 at 20°, and m_{Na} 25·76. The *picrolonate*, $C_4H_{11}ON,C_{10}H_8O_5N_4$, crystallises in stout, yellow prisms and melts and decomposes at 204°; the *picrate*, $C_4H_{11}ON,C_6H_3O_7N_3$, forms stout, yellow crystals, and sinters and melts

at 122°; the *hydrochloride*, $C_4H_{11}ON,HCl$, crystallises in shimmering, white leaflets and is deliquescent; the *platinichloride*,

$$(C_4H_{11}ON)_2,H_2PtCl_6,$$

crystallises in long, hair-like needles and melts and decomposes at 192°. The *carbamide*, $NH_2{\cdot}CO{\cdot}NH{\cdot}C_2H_4{\cdot}OEt$, forms an oil which solidifies to a crystalline, colourless mass when cooled and stirred with ether; it sinters at 53°, melts at 56°, and is very soluble in water or alcohol. The *phenylcarbamide*, $NHPh{\cdot}CO{\cdot}NH{\cdot}C_2H_4{\cdot}OEt$, crystallises from a mixture of benzene and light petroleum in white needles and melts at 68—70°. The *phenylthiocarbamide*, $NHPh{\cdot}CS{\cdot}NH{\cdot}C_2H_4{\cdot}OEt$, crystallises from alcohol in white needles and melts at 112°.

Aminoethyl ether interacts with acetylacetone with development of heat and formation of the *anhydride*, $C_9H_{17}O_2N$, which forms a yellow oil possessing a fruity odour and boiling at 254° under 752 mm. pressure. With acetonylacetone, aminoethyl ether interacts to form the *pyrrole* derivative, $\begin{matrix}CH{:}CMe\\ |\\ CH{:}CMe\end{matrix}\!\!>\!N{\cdot}C_2H_4{\cdot}OEt$, which is obtained as a yellow oil, boiling at 225—226° under 751 mm. pressure and giving the pine-wood reaction.

Methylchloroethylamine hydrochloride (Marckwald and Frobenius, Abstr., 1902, i, 23) can be prepared by heating methylaminoethyl alcohol with fuming hydrochloric acid at 160—170°; the *aurichloride*, $C_3H_8NCl,HAuCl_4$, crystallises in yellow needles and melts at 126°; the *bismuthoiodide* crystallises in purple, hexagonal prisms and melts at 208°.

Methylbromoethylamine hydrobromide, prepared by heating methylaminoethyl alcohol with hydrobromic acid of sp. gr. 1·49 at 160°, crystallises from alcohol and sinters and melts at about 80° (compare Marckwald, *loc. cit.*).

Methylaminoethyl ether, $NHMe{\cdot}CH_2{\cdot}CH_2{\cdot}OEt$, is formed along with methylethylenimine and dimethylpiperazine by the action of alcoholic sodium ethoxide on methylchloroethylamine hydrochloride or methylbromoethylamine hydrobromide at 160°, or alone by the action of absolute alcohol on the amine salts at 160°. It is obtained as a mobile liquid, which boils at 114—115° under 744 mm. pressure and has the sp. gr. 0·8363 at 20°/4°, n_D 1·4147, and $\mathfrak{M}_{na}$ 30·82. It has an amine-like odour and an alkaline reaction, and is miscible in all proportions with water, alcohol, or ether. The salts are easily soluble, and crystallise only from concentrated solutions; the *aurichloride*, $C_5H_{13}ON,HAuCl_4$, crystallises in long, yellow needles and melts at 127°; the *platinichloride*, $(C_5H_{13}ON)_2,H_2PtCl_6$, forms needles and melts and decomposes at 208°; the *picrate*, $C_5H_{13}ON,C_6H_3O_7N_3$, crystallises in concentric aggregates of prisms and melts at 119°; the *picrolonate*, $C_5H_{13}ON,C_{10}H_8O_5N_4$, crystallises in yellow needles, blackens at 109°, and melts at 111°. The *phenylthiocarbamide*, $NHPh{\cdot}CS{\cdot}NMe{\cdot}CH_2{\cdot}CH_2{\cdot}OEt$, separates from alcohol in brown crystals and melts at 78—80°.

A table is given showing the melting points, sp. gr., and refractive indexes of amino-, methylamino-, and dimethylamino-ethyl alcohol and of the three corresponding ethers. G. Y.

Metastable States in Reactions between Gaseous and Solid Substances. HEINRICH LEY and G. WIEGNER (*Zeit. Elektrochem.*, 1905, **11**, 585—593).—When copper aminoacetate is exposed to dry ammonia gas, it takes up two molecules of ammonia. The compound has a dissociation pressure of less than 100 mm. at the ordinary temperature, notwithstanding which the combination of the copper aminoacetate with ammonia at atmospheric pressure takes place at first extremely slowly; after a considerable period of induction, the reaction starts suddenly, and then goes on with constant velocity until it is complete. The length of the initial period depends on the dryness of the salt; a trace of moisture (other than water of crystallisation) diminishes the initial period very considerably; for example, the reaction began after 63 hours with a very carefully dried sample, whilst with another containing water of crystallisation it began in six minutes. During the initial period, nuclei of the ammonia compound appear to be formed; these can sometimes be seen owing to the difference in colour. T. E.

Synthesis of Amino-acids. V. α-Amino-δ-hydroxyvaleric Acid. S. P. L. SÖRENSEN (*Chem. Centr.*, 1905, ii, 398—401; from *Compt. rend. trav. Labor. Carlsberg, Copenhagen*, 1905, **6**, 137—192. Compare Abstr., 1903, i, 833).—Ethyl sodiophthaliminomalonate, on treatment with trimethylene dibromide, gives *ethyl γ-bromopropylphthaliminomalonate*, $C_3H_6Br\cdot C(CO_2Et)_2\cdot N<^{CO}_{CO}>C_6H_4$; from this, the corresponding acetyl derivative, $OAc\cdot C_3H_6\cdot C(CO_2Et)_2\cdot N<^{CO}_{CO}>C_6H_4$, may be prepared by the action of potassium acetate.

This acetyl derivative on hydrolysis breaks up in two ways, yielding as the chief product the hydrochloride of α-amino-δ-hydroxyvaleric acid and a much smaller quantity of pyrrolidine-2-carboxylic acid, together with some glycine hydrochloride.

α-Amino-δ-hydroxyvaleric acid, $OH\cdot[CH_2]_3\cdot CH(NH_2)\cdot CO_2H$, crystallises from 80 per cent. alcohol in colourless needles or plates and melts and decomposes at 223—224° (corr.). The acid is readily soluble in water, soluble in aqueous alcohol, slightly soluble in absolute alcohol and acetone, and practically insoluble in ether or light petroleum. On heating at 195—200°, it yields pyrrolidine-2-carboxylic acid, together with other decomposition products. A 35 per cent. yield of this acid is obtained on heating with concentrated hydrochloric acid at 150°.

Glycine is very readily isolated by means of phosphotungstic acid. The same reagent may also be used for the separation of α-amino-δ-hydroxyvaleric acid from pyrrolidine-2-carboxylic acid, since with a 5 per cent. solution of the former it only gives a crystalline precipitate of white needles after 24 hours, whereas with the latter, in 0·5 per cent. solution, it gives at once a characteristic precipitate consisting of short, rhombohedral prisms.

In the esterification of α-amino-δ-hydroxycarboxylic acid by Fischer's method, a portion of the acid is transformed into pyrrolidine-2-

carboxylic acid. The ester is only partially extracted by ether, and when a mixture of the esters of the two acids is distilled, only the pyrrolidinecarboxylic ester distils unchanged, the ester of the other acid undergoing complete decomposition.

Allylglycine was prepared with the object of determining whether it could be converted into pyrrolidine-2-carboxylic acid:

$$CH_2{:}CH{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H \longrightarrow CH_2{<}\begin{matrix} CH_2{\cdot}CH_2 \\ NH{-}CH{\cdot}CO_2H \end{matrix},$$

but the conversion was not achieved. Allylglycine forms rhombohedral plates; it has a sweet taste and melts and evolves gas at 250—252° (corr.); the substance is fairly soluble in water and practically insoluble in absolute alcohol; it is not precipitated by phosphotungstic acid, although after 24 hours prismatic crystals of some salt are deposited which are readily soluble in water and in alcohol. P. H.

Oxidation Products of Glycylglycine. LEO POLLAK (*Beitr. chem. Physiol. Path.*, 1905, **7**, 16—20).—Glycylglycine (Fischer, Abstr., 1901, i, 675), when oxidised with calcium permanganate at 0°, yields oxalylaminoacetic acid (Kerp and Unger, Abstr., 1897, i, 269), which is hydrolysed by hydrochloric acid into oxalic acid, ammonia, and probably acetic acid. J. J. S.

Preparation of Taurocholic Acid. IVAR BANG (*Beitr. chem. Physiol. Path.*, 1905, **7**, 148—149. Compare Hammarsten, this vol., i, 33).—Pure taurocholic acid may be obtained from ox-bile by the following process. The bile is added to an equal volume of albumin, diluted with 4 to 5 volumes of water and containing hydrochloric acid in order to dissolve globulins. The precipitated albumin taurocholate is removed and washed until the filtrate no longer gives Pettenkofer's test for glycocholic acid. The precipitate is mixed with 2 per cent. hydrochloric acid, well shaken, filtered, and the filtrate saturated with sodium chloride. Any small amounts of albumin are removed and the clear solution mixed with ether and well shaken, when the taurocholic acid begins to crystallise. J. J. S.

Constitution of the Fulminuric Acids. CELSO ULPIANI (*Gazzetta*, 1905, **35**, ii, 7—18).—The compound $(CHON)_n$, obtained by the action of concentrated ammonia solution on the peroxide of ethyl oximinoacetate (compare Ulpiani and Bernardini, Abstr., 1904, i, 971), is shown to be succinamide dinitrosoperoxide, $\begin{matrix} NH_2{\cdot}CO{\cdot}C{:}NO \\ NH_2{\cdot}CO{\cdot}C{:}NO \end{matrix}$. When boiled with concentrated ammonia solution, it yields (1) the fulminuric acid obtained by Liebig by the action of alkali chlorides on mercuric fulminate, to which the authors ascribe the constitution $NO_2H{:}C(CN){\cdot}CO{\cdot}NH_2$; (2) *β-iso*fulminuramide, $\begin{matrix} NH_2{\cdot}C{:}N \\ NH_2{\cdot}CO{\cdot}C{:}N \end{matrix}{>}O$, and, as a result of the subsequent hydrolysis of this compound, (3) *β-iso*fulminuric acid, previously obtained by Scholvien (Abstr., 1886 137) by the action of dilute sulphuric acid on sodium fulminate. The first step in the action of ammonia on succinamide dinitrosoperoxide is

probably the formation of the unstable compound,

$$NH_2\cdot CO\cdot C\lessdot_{NO}^{CH}\!\!>NO,$$

which subsequently undergoes further changes, yielding the compounds enumerated above.

β-iso*Fulminuramide*, $C_3H_4O_2N_4$, separates from water in shining, prismatic crystals melting at 175°, has a neutral reaction, and is practically insoluble in organic solvents. On boiling with alkalis, it gives up ammonia, but it is stable towards mineral acids. When boiled with barium hydroxide solution, it is completely transformed into barium β-*iso*fulminurate with evolution of ammonia, and it apparently bears the same relation to β-*iso*fulminuric acid as its isomeride described by Ehrenberg (Abstr., 1885, 38) does to *iso*fulminuric acid. T. H. P.

Imino-*CC*-dialkylbarbituric Acids. (5 : 5-Dialkylmalonylguanidines.) Firma Emanuel Merck (D.R.-P. 158890. Compare Abstr., 1904, i, 380 ; this vol., i, 670—671).—Dialkylmalonyl chlorides react with guanidine in alcoholic solution without the application of heat, forming iminodialkylbarbituric acids (dialkylmalonylguanidines).

5 : 5-*Diethylmalonylguanidine*, $NH{:}C<^{NH\cdot CO}_{NH\cdot CO}>CEt_2$, forms colourless needles or feathery groups of crystals, and decomposes without melting when heated. The *dipropyl* and *dimethyl* derivatives are similar. Acids readily hydrolyse them to the corresponding dialkylbarbituric acids. C. H. D.

Iminobarbituric and Barbituric Acids. Max Conrad (*Annalen*, 1905, **340**, 310—325. Compare Michael, Abstr., 1887, 716 ; Traube, Abstr., 1900, i, 416 ; 1901, i, 54 ; 1904, i, 632 ; Merck, Abstr., 1904, i, 380 ; this vol., i, 671 ; Fischer and Dilthey, this vol., i, 35).—In presence of sodium ethoxide, ethyl cyanoacetate and carbamide or thiocarbamide react at the laboratory temperature, and ethyl alkyl- or dialkyl-cyanoacetates and carbamide when warmed, to form iminobarbituric and substituted iminobarbituric acids. These, when heated with mineral acids or formic or acetic acid, are converted into the corresponding barbituric acids. At the laboratory temperature, ethyl cyanodialkylacetates and carbamide react in presence of sodium ethoxide to form cyanodialkylacetylcarbamides. 4-Iminomalonylthiocarbamide (4-amino-6-oxy-2-thiopyrimidine) does not melt at 310°. 4-Iminomalonylguanidine (2 : 4-diamino-6-oxypyrimidine) melts and decomposes at 286°. 4-Iminomalonyl-3-methylcarbamide (4-amino-2 : 6-dioxy-3-methylpyrimidine) crystallises in hexagonal leaflets and melts and decomposes at 305°. *Malonylmethylcarbamide*, $CH_2<^{CO\cdot NMe}_{CO-NH}>CO$, forms colourless crystals, melts at 133°, and gives the violuric acid reaction with potassium nitrite. 4-*Imino*-5-*propylmalonylcarbamide*, $CHPr<^{C(NH)\cdot NH}_{CO\text{——}NH}>CO$, crystallises in glistening, white leaflets, melts and decomposes above 300°, is soluble in hot alcohol or glacial acetic acid, and has both acid and basic properties.

4-*Imino*-5 : 5-*diethylmalonylcarbamide* (*iminoveronal*),

$$CEt_2<\begin{matrix}C(NH)\cdot NH\\ CO\text{——}NH\end{matrix}>CO,$$

crystallises from water in colourless prisms, melts and decomposes at 295°, and is soluble in aqueous alkali hydroxides or acids; the *hydrochloride*, $C_8H_{13}O_2N_3,HCl$, is crystalline.

Ethyl cyanoethylpropylacetate [*a-cyano-a-ethylvalerate*],

$$CN\cdot CEtPr\cdot CO_2Et,$$

formed by the action of ethyl iodide and sodium ethoxide on ethyl cyanovalerate, boils at 226—229° and has a sp. gr. 0·952 at 15°. 4-*Imino-5-ethyl-5-propylmalonylcarbamide*, $CEtPr<\begin{matrix}C(NH)\cdot NH\\ CO\text{——}NH\end{matrix}>CO$, melts and decomposes at 301°.

Ethyl dipropylcyanoacetate [*a-cyano-a-propylvalerate*],

$$CN\cdot CPr_2\cdot CO_2Et,$$

prepared by adding propyl iodide to a solution of ethyl cyanoacetate in alcoholic sodium ethoxide, is purified from ethyl cyanoacetate and cyanovalerate by treatment with concentrated aqueous ammonia, with which the latter form soluble amides. It boils at 241—242° and has a sp. gr. 0·937 at 16°/15°. 4-*Imino*-5 : 5-*dipropylmalonylcarbamide*,

$$CPr_2<\begin{matrix}C(NH)\cdot NH\\ CO\text{——}NH\end{matrix}>CO,$$

crystallises in short prisms and melts and decomposes at 305°. Dipropylbarbituric acid melts at 166° (m. p. 145°; Fischer and Dilthey, *loc. cit.*). 4-*Imino*-5 : 5-*dibenzylmalonylcarbamide*,

$$C(CH_2Ph)_2<\begin{matrix}C(NH)\cdot NH\\ CO\text{——}NH\end{matrix}>CO,$$

melts and decomposes at 295°, and is soluble in dilute hydrochloric acid, from its solution in which it is precipitated on addition of ammonia.

4-Imino-5 : 5-diethylmalonylguanidine, $CEt_2<\begin{matrix}C(NH)\cdot NH\\ CO\text{——}NH\end{matrix}>C:NH$, formed by warming guanidine hydrochloride with ethyl cyanoethylbutyrate and sodium ethoxide in alcoholic solution, crystallises in long prisms and melts and decomposes at 297° (compare Merck, this vol., i, 670). 4-*Imino*-5-*ethyl*-5-*propylmalonylguanidine*, when boiled with dilute hydrochloric acid, is converted into 5-*ethyl*-5-*propylmalonylguanidine*, $CEtPr<\begin{matrix}CO\cdot NH\\ CO\cdot NH\end{matrix}>C:NH$, which crystallises in long, colourless needles, and when boiled with nitric acid or heated with hydrochloric acid at 120—140° yields 5-ethyl-5-propylbarbituric acid. 4-*Imino*-5 : 5-*diethylmalonylthiocarbamide*, $CEt_2<\begin{matrix}C(NH)\cdot NH\\ CO\text{——}NH\end{matrix}>CS$, crystallises in yellow prisms, melts and decomposes at 255°, and is converted by boiling dilute hydrochloric acid into 2-thio-5 : 5-diethylbarbituric acid. This is oxidised by boiling nitric acid of sp. gr. 1·22 to 5 : 5-diethylbarbituric acid. G. Y.

Iminodialkylmalonylalkyl- and Iminodialkylmalonylphenylcarbamides. MAX CONRAD and A. ZART (*Annalen*, 1905, **340**, 326—335. See preceding abstract).—4-*Imino*-1-*methyl*-5 : 5-*diethyl*-

barbituric acid, $CEt_2<\genfrac{}{}{0pt}{}{C(NH)\cdot NH}{CO\text{——}NMe}>CO$, is formed by boiling 4-imino-5 : 5-diethylmalonylcarbamide with methyl iodide and sodium ethoxide in alcoholic solution. It crystallises in rhombic leaflets, melts at 258°, is converted into 1-methyl-5 : 5-diethylbarbituric acid (Fischer and Dilthey, this vol., i, 36) when boiled with dilute mineral acids, and when heated with alcoholic sodium ethoxide in a sealed tube at 150—160° is decomposed into ammonia, carbon dioxide, and *cyano-ethylbutyromethylamide,* $CN\cdot CEt_2\cdot CO\cdot NHMe$, which crystallises in long prisms and melts at 102°.

4-*Imino*-3-*methyl*-5 : 5-*diethylbarbituric acid,*

$$CEt_2<\genfrac{}{}{0pt}{}{C(NH)\cdot NMe}{CO\text{———}NH}>CO,$$

is formed by warming methylcarbamide or acetylmethylcarbamide with ethyl cyanoethylbutyrate and sodium ethoxide in alcoholic solution. It crystallises in needles, melts at 145°, and yields 1-methyl-5 : 5-diethylbarbituric acid when boiled with dilute mineral acids, and cyanoethylbutyramide, melting at 121°, when heated with sodium ethoxide.

4-*Methylimino*-1-*methyl*-5 : 5-*diethylbarbituric acid,*

$$CEt_2<\genfrac{}{}{0pt}{}{C(NMe)\cdot NH}{CO\text{———}NMe}>CO,$$

is obtained by boiling 4-imino-1-methyl-5 : 5-diethylbarbituric acid with methyl iodide and sodium ethoxide in absolute alcoholic solution for 8 hours in a reflux apparatus. It crystallises in hexagonal plates, melts at 212°, and is hydrolysed by boiling dilute hydrochloric acid with formation of methylamine and 1-methyl-5 : 5-diethylbarbituric acid.

4-*Imino*-1 : 3-*dimethyl*-5 : 5-*diethylbarbituric acid,*

$$CEt_2<\genfrac{}{}{0pt}{}{C(NH)\cdot NMe}{CO\text{———}NMe}>CO,$$

is formed by heating the sodium salt of 4-imino-3-methyl-5 : 5-diethylbarbituric acid with methyl iodide or methyl sulphate in aqueous alcoholic solution. It crystallises in hexagonal leaflets, melts at 40°, and forms a crystalline *hydriodide* and a *platinichloride,*

$$(C_{10}H_{17}N_3)_2,H_2PtCl_6,$$

which crystallises in short, orange prisms. When heated with hydrochloric acid in a sealed tube at 120°, it yields 1 : 3-*dimethyl*-5 : 5-*diethylbarbituric acid,* which forms prismatic crystals and melts at 38°.

4-*Imino*-1-*phenyl*-5 : 5-*diethylbarbituric acid,*

$$CEt_2<\genfrac{}{}{0pt}{}{C(NH)\cdot NH}{CO\text{——}NPh}>CO,$$

formed by warming phenylcarbamide with ethyl cyanoethylbutyrate and sodium ethoxide in alcoholic solution, crystallises in glistening, white prisms, melts at 222°, and when boiled with 20 per cent. hydrochloric acid is converted into 1-phenyl-5 : 5-diethylbarbituric acid melting at 175° (m. p. 197°; Fischer and Dilthey, *loc. cit*). When heated with sodium ethoxide, 4-imino-1-phenyl-5 : 5-diethylbarbituric acid is hydrolysed to *cyanoethylbutyranilide,* $CN\cdot CEt_2\cdot CO\cdot NHPh$, which crystallises in long, delicate needles and melts at 122°.

G. Y.

Cyanodialkylacetylcarbamides and the Amides of Substituted Malonic and Cyanoacetic Acids. Max Conrad and A. Zart (*Annalen*, 1905, **340**, 335—350. Compare preceding abstracts; Mulder, Abstr., 1878, 786; Errera, Abstr., 1896, i, 528).—*a-Cyano-a-ethylbutyrylcarbamide*, $CN·CEt_2·CO·NH·CO·NH_2$, is formed by the action of ethyl cyanoethylbutyrate and sodium ethoxide on carbamide in alcoholic solution at the ordinary temperature, treatment of the product with glacial acetic acid, and removal of the small amount of iminodiethylbarbituric acid which is formed, by shaking with dilute hydrochloric acid or by boiling with ethyl acetate. It crystallises in white prisms or needles, melts at 118°, and when heated with sodium ethoxide or concentrated sodium hydroxide is converted into 4-imino-5 : 5-diethylbarbituric acid. *Diethylmalonuramide*, $NH_2·CO·CEt_2·CO·NH·CO·NH_2$, is formed along with diethylbarbituric and ureidodiethylmalonic (Fischer and Dilthey, this vol., i, 37) acids, when cyanoethylbutyrylcarbamide is warmed with sulphuric or nitric acid and the product treated with ammonia. It crystallises in colourless prisms and melts at 199°. Ureidodiethylmalonic acid melts with evolution of carbon dioxide and formation of ethylbutyrylcarbamide at 163°. Cyanoethylbutyramide is formed when cyanoethylbutyrylcarbamide or 4-imino-5 : 5-diethylbarbituric acid is heated with alcoholic sodium hydroxide or sodium ethoxide at 120°. It yields diethylmalonamide (Fischer and Dilthey, Abstr., 1902, i, 269) when warmed at 100° for some hours with sulphuric acid and a little water. This sublimes in long, flat needles and boils with slight decomposition above 360°.

The action of sodium on a mixture of ethyl cyanoethylbutyrate and urethane leads to the formation of *a-cyano-a-ethylbutyrylurethane*, $CN·CEt_2·CO·NH·CO_2Et$, which crystallises in long, thin prisms, melts at 128°, and when warmed with concentrated sulphuric acid decomposes into carbon dioxide and diethylmalonamide.

Cyanovaleramide was obtained on treating crude ethyl cyanopropylvalerate with concentrated ammonia. It melts at 122° (m. p. 118°; Henry, *Jahresber.*, 1889, 639), and when warmed with sulphuric acid yields propylmalonamide melting at 183°.

a-Cyano-a-propylvalerylcarbamide, $CN·CPr_2·CO·NH·CO·NH_2$, is obtained by treating carbamide with ethyl cyanopropylvalerate in presence of sodium ethoxide. It crystallises in colourless prisms, melts at 101°, and when warmed with sulphuric acid yields dipropylbarbituric acid and *dipropylmalonuramide*, $NH_2·CO·CPr_2·CO·NH·CO·NH_2$, which crystallises in slender prisms and melts at 207°.

Cyanopropylvaleramide (Errera, *loc. cit.*) is obtained in similar manner to cyanoethylbutyramide. It melts at 153° and is converted by warming with concentrated sulphuric acid into dipropylmalonamide melting at 214°.

a-Cyano-a-ethylvaleramide, obtained as a by-product in the preparation of 4-imino-5-ethyl-5-propylbarbituric acid, melts at 116°.

The following dibenzyl derivatives were prepared in the same manner as the diethyl compounds: *cyanodibenzylacetylcarbamide*, $CN·C(CH_2Ph)_2·CO·NH·CO·NH_2$, melts at 187°; *cyanodibenzylacetamide* crystallises in prisms and melts at 165°; *dibenzylmalonamide* crystallises in glistening leaflets and melts at 193°.

The action of sodium ethoxide and ethyl cyanoethylbutyrate on methylcarbamide at the laboratory temperature leads to the formation of *cyanoethylbutyrylmethylcarbamide*, $CN\cdot CEt_2\cdot CO\cdot NH\cdot CO\cdot NHMe$, which crystallises in thick, rhombic leaflets, melts at 153°, is not soluble in dilute hydrochloric acid, and when heated with sodium ethoxide at 50—60° yields 4-imino-3-methyl-5 : 5-diethylbarbituric acid, but at 120—130° is converted into cyanodiethylacetamide.

Cyanoethylbutyrylphenylcarbamide, $CN\cdot CEt_2\cdot CO\cdot NPh\cdot CO\cdot NH_2$, crystallises in long, flat prisms, melts at 156°, is insoluble in hydrochloric acid, and when heated with sodium ethoxide in a sealed tube at 130—150° decomposes to ammonia and cyanoethylbutyramide, which is formed also by the action of sodium ethoxide and ethyl cyanoethylbutyrate on aniline and treatment of the product with acetic acid. When warmed with sulphuric acid, this is converted into the anilide and the sulphanilide of malonamic acid. The *anilide*, $NH_2\cdot CO\cdot CEt_2\cdot CO\cdot NHPh$, crystallises in white prisms, melts at 132°, and is precipitated from its solution in sulphuric acid immediately on dilution. The *sulphanilide*, $NH_2\cdot CO\cdot CEt_2\cdot CO\cdot NH\cdot C_6H_4\cdot SO_3H$, separates from the dilute acid solution after one or two days as a white, crystalline mass, has a strong acid reaction, and decomposes carbonates. *Diethylmalonanilic acid*, $NHPh\cdot CO\cdot CEt_2\cdot CO_2H$, obtained by hydrolysis of the amide by means of potassium hydroxide and precipitation of the acid with hydrochloric acid, melts at 105° and decomposes to diethylacetanilide and carbon dioxide at 140°.

Ethyl diethylmalonamate, $NH_2\cdot CO\cdot CEt_2\cdot CO_2Et$, formed by hydrolysis of ethyl cyanoethylbutyrate by means of sulphuric acid, crystallises in needles or large prisms, melts at 79°, and boils without decomposition at 263°.

Hydrolysis of the ester with alcoholic sodium hydroxide leads to the formation of *diethylmalonamic acid*, $NH_2\cdot CO\cdot CEt_2\cdot CO_2H$, which crystallises in stellate groups of needles and melts and decomposes into carbon dioxide and ethylbutyramide at 146°. It is formed also by warming cyanoethylbutyric acid (Hesse, Abstr., 1897, i, 17) with concentrated sulphuric acid.

Ethyl dipropylmalonamate, $NH_2\cdot CO\cdot CPr_2\cdot CO_2Et$, forms crystals, melts at 92°, and forms, as does also the diethylmalonamate, the corresponding barbituric acid when treated with carbamide and sodium ethoxide. G. Y.

Electrolysis of Imides. ERNESTO PANNAIN (*Gazzetta*, 1905, **35**, ii, 94—100).—When an alkaline derivative of an imide is electrolysed under the conditions employed by the author, the imide, $R<\substack{CO\\CO}>NH$, is first transformed into the corresponding amino-acid,

$$NH_2\cdot CO\cdot R\cdot CO_2H,$$

the latter then being hydrolysed to the ammonium salt of the dibasic acid, $CO_2NH_4\cdot R\cdot CO_2H$, which is then resolved by the current into ammonia and the acid. Thus, in potassium hydroxide solution, phthalimide yields phthalic acid, succinimide, and succinic acid at the anode. T. H. P.

Preparation of Mono- and Di-bromoacetonitrile. Wilhelm Steinkopf (*Ber.*, 1905, **38**, 2694—2696).—Bromoacetonitrile (Henry, Abstr., 1886, 1001), boiling at 60—62° under 24 mm. pressure, is formed by the distillation in a vacuum of a mixture of bromoacetamide and phosphoric oxide. The action of chloroacetonitrile on potassium bromide leads to the formation of a product containing only 65·4 instead of 66·67 per cent. of bromine.

Contrary to the statement of van't Hoff (this Journal, 1875, 357), the action of bromine on ethyl cyanoacetate leads to the formation of dibromoacetamide, together with a small quantity of a *substance* melting at 86°. Dibromoacetonitrile is formed by distilling in a vacuum a mixture of dibromoacetamide and phosphoric oxide. It is a yellow oil, which has a suffocating odour, attacks the eyes, and boils at 67—69° under 24 mm. pressure. G. Y.

Source of the Excessive Moisture found in certain Combustions. Joseph A. Muller (*Bull. Soc. chim.*, 1905, [iii], **33**, 953—954).—The author describes a number of experiments which show that the source of the water obtained on combustion of certain ferrocyanides and carbonylferrocyanides is the substance burnt, and not errors in the method of combustion. These ferrocyanides and carbonylferrocyanides retain therefore small percentages of water even when dried at 125°. G. Y.

Blue Iron-cyanogen Compounds. II. Karl A. Hofmann and F. Resenscheck (*Annalen*, 1905, **340**, 267—275. Compare Hofmann, Heine, and Höchtlen, this vol., i, 38).—In a neutral solution, a molecular mixture of ferrous sulphate and potassium ferrocyanide forms a white precipitate which is oxidised by the air to a blue soluble in water, but differing from soluble Prussian blue in its behaviour towards oxalic acid. If the white precipitate is formed in presence of 1 per cent. of sulphuric acid, it is more stable towards atmospheric oxygen, and when oxidised forms a stable, soluble blue, which, except for small differences in the content of water, has the same empirical formula, $KFeFeCy_6,H_2O$, as soluble Prussian blue and Williamson's violet. This new blue, after being dried over sulphuric acid and finally over phosphoric oxide, is soluble in water or 10 per cent. oxalic acid, forming blue solutions; on addition of ammonia to the aqueous solution, there is formed after some minutes a blue precipitate which becomes green and finally changes into reddish-brown ferric hydroxide; the filtrate from this contains potassium ferrocyanide but no ferricyanide. On addition of 10 per cent. hydrochloric acid to the aqueous solution, a blue, flocculent precipitate is formed slowly; this is not soluble in water, but behaves like the parent substance towards oxalic acid and ammonia. With ferric chloride, the aqueous solution yields slowly a blue, flocculent precipitate which is soluble in water and is apparently the unchanged soluble blue. In aqueous solution, this stable soluble blue is dissolved in the colloidal state, as shown by the freezing point of the solution being that of water, and by the fact that in an electrical field it travels towards the anode. The optical

properties of the aqueous solution point to the molecule of the new blue as being greater than that of the ordinary soluble blue.

Soluble Prussian blue is soluble in water or oxalic acid even after being dried for some months, but loses its solubility in water when heated at 100° for some hours. It is decomposed to ferric hydroxide and potassium ferrocyanide by 4 per cent. aqueous ammonia in a few seconds, and forms insoluble Prussian blue immediately on addition of ferric chloride. Dilute acids, such as $1\frac{1}{2}$ per cent. sulphuric acid, remove the alkali from soluble Prussian blue, the residue after drying having the composition $2Fe_2H(CN)_6,3H_2O$ and being insoluble in water but soluble in 10 per cent. oxalic acid.

Williamson's violet does not dissolve in water or oxalic acid, but forms a suspension which is greenish-blue by transmitted, dark purple by reflected, light. It is decomposed by 4 per cent. ammonia after some hours into ferric hydroxide and alkali ferrocyanide, but is not acted on by dilute acids or by aqueous ferric chloride on prolonged digestion.

The following constitutional formulæ are suggested: for soluble Prussian blue, $Fe(OH)_2KH_2Fe(CN)_6$; for Williamson's violet, $KFe(CN)_6{<}{\substack{Fe\\Fe}}{>}Fe(CN)_6K$, the water always present being probably also constitutional; and for the new soluble stable blue,

$$Fe(CN)_6{<}{\substack{Fe\\Fe}}{>}Fe(CN)_6K_2.$$

A blue, $Fe_7(CN)_{18},10H_2O$, having properties similar to those of Williamson's violet, but being less stable towards dilute ammonia, is formed by reducing a mixture of ferric ammonium alum and potassium ferricyanide by means of hydrogen peroxide in presence of free hydrochloric acid. G. Y.

Action of Ketone Reagents on Sodium Carbonylferrocyanide. JOSEPH A. MULLER (*Bull. Soc. chim.*, 1905, [iii], **33**, 945—951. Compare Abstr., 1904, i, 147).—Sodium carbonylferrocyanide is not reduced by sodium and absolute alcohol, or by aluminium and acetic acid, or by sodium amalgam and water.

If an aqueous solution of 2 mols. of semicarbazide and 1 mol. of sodium carbonylferrocyanide is evaporated to dryness at 55° and the residue washed with absolute alcohol, the *compound*

$$2Na_3FeC(N{\cdot}CO{\cdot}N_2H_3)(CN)_5$$

is obtained as a white, crystalline powder, which is easily soluble in water. With cobalt salts, the aqueous solution yields a lilac precipitate, with ferric salts a violet precipitate which rapidly changes into the bluish-violet ferrosoferric compound, and with cupric salts a green precipitate, which changes into the colourless cuprous salt. If a molecular solution of sodium carbonylferrocyanide and semicarbazide is evaporated to dryness, the product obtained on washing the residue with alcohol is practically the unchanged sodium salt.

Hydroxylamine has no action on sodium carbonylferrocyanide in aqueous or slightly alkaline solution at 100—105°, or in alcoholic sodium ethoxide solution at 170°. But if the sodium salt is boiled with hydroxylamine hydrochloride and an excess of sodium hydroxide

in sufficiently concentrated solution, there is produced a yellow coloration which becomes intensely red and is due probably to formation of the *sodium* salt of the unstable oxime, $Na_3FeC(N\cdot ONa)(CN)_5$. In moderately alkaline solution, the red colour disappears slowly at the ordinary temperature, quickly on heating, sodium ferrocyanide and a small quantity of ferric oxide being formed. The red colour disappears on acidification with a strong acid, more slowly with a weak acid, and reappears, but less strongly, if the solution is made immediately alkaline. No coloration is formed if the carbonylferrocyanide is replaced by the ferrocyanide or if it is boiled with sodium hydroxide only (compare Simon, Abstr., 1904, ii, 84). On heating sodium carbonylferrocyanide with hydrazine hydrate and sodium hydroxide at 50—55° and washing the residue with alcohol, there is obtained a yellow powder which is easily soluble in water to form a solution which becomes red on heating, and when treated with acetic acid yields sodium carbonylferrocyanide and ferrocyanide and a small quantity of Prussian blue.

No condensation products could be obtained by heating the carbonylferrocyanide with hydrazine, phenylhydrazine, or phenylmethylhydrazine acetates with or without the addition of sodium acetate.

G. Y.

Preparation of Barium Cacodylate. ANGELO ANNONI (*Chem. Centr.*, 1905, ii, 751; from *Boll. Chim. Farm.*, 1905, **44**, 485—488).—In a pure form, the substance can be obtained by pounding together equal parts of crystallised barium hydroxide and cacodylic acid and adding baryta water until the solution reacts feebly alkaline. The decanted and filtered solution is then neutralised with cacodylic acid and evaporated in a vacuum, the residue being afterwards heated for several hours at 115—120° over a mixture of potassium hydroxide, lime, and calcium chloride. H. M. D.

Tetra-alkylarsonium Bases. EMIL MANNHEIM (*Annalen*, 1905, **341**, 182—233).—The hexa-alkyldiarsonium bases were prepared by Partheil, Amort, and Gronover (Abstr., 1898, i, 351; 1899, i, 474) by the action of alkyl iodides on mercury arsenide. A series of the double salts of the tetra-alkylarsonium bases have been studied and compared with the double salts of the bases prepared according to the directions of the authors just mentioned. It was thus shown that tetra-alkylarsonium bases are formed in this reaction and not hexa-alkyldiarsonium bases, which do not therefore appear to exist.

The following double salts of tetramethylarsonium hydroxides have been prepared: the *compound* $AsMe_4I,HgI_2$ crystallises in yellow needles melting at 184°; the *compound* $AsMe_4Cl,HgCl_2$ crystallises in white needles melting at 175—176°; the *platinichloride*,

$$(AsMe_4Cl)_2PtCl_4,$$

forms yellow crystals decomposing at 250—260°; the *aurichloride*, $AsMe_4Cl,AuCl_3$, crystallises in needles melting at 233°. The double salts derived from tetraethylarsonium hydroxide were prepared: the *compound* $AsEt_4I,HgI_2$ crystallises in yellow needles melting at 112°; the *compound* $AsEt_4Cl,HgCl_2$ crystallises in white needles melting at 139°; the *platinichloride*, $(AsEt_4Cl)_2PtCl_4$, forms crystals melting and

decomposing at 224°; the *aurichloride*, $AsEt_4Cl,AuCl_3$, crystallises in yellow needles melting at 171°. The double salts derived from tetra-*n*-propylarsonium hydroxide are :—$AsPr^{\alpha}_4I,HgI_2$ crystallises in needles melting at 120°; the *compound* $AsPr^{\alpha}_4Cl,HgCl_2$ crystallises in white needles melting at 169°; the *platinichloride*, $(AsPr^{\alpha}_4Cl)_2PtCl_4$, forms reddish-yellow crystals melting at 189°; the *aurichloride*, $AsPr^{\alpha}_4Cl,AuCl_3$, crystallises in needles melting at 127°. *Tetra*iso*propylarsonium iodide*, $AsPr^{\beta}_4I$, is prepared by heating arsenic with *iso*propyl iodide for thirty hours at 180° and crystallises in needles with no definite melting point. The following double salts derived from tetra*iso*propylarsonium hydroxide were prepared: the *compound* $AsPr^{\beta}_4I,HgI_2$ crystallises in yellow needles melting at 114°; the *compound* $AsPr^{\beta}_4Cl,HgCl_2$ crystallises in needles melting at 171°; the *platinichloride*, $(AsPr^{\beta}_4Cl)_2PtCl_4$, forms crystals and decomposes at 211°; the *aurichloride*, $AsPr^{\beta}_4Cl,AuCl_3$, crystallises in slender needles melting at 186—188°.

Tetra-n-*butylarsonium iodide*, $As(C_4H_9)I$, forms crystals without any definite melting point. The double salts derived from tetra-*n*-butylarsonium hydroxide were prepared: the *compound* $As(C_4H_9)_4I,HgI_2$ crystallises in yellow needles melting at 109°; the *platinichloride*,

$$[As(C_4H_9)_4Cl]_2PtCl_4,$$

forms yellowish-red crystals decomposing at 220°; the *aurichloride*, $As(C_4H_9)_4Cl,AuCl_3$, crystallises in needles melting at 131°.

Tetrabenzylarsonium chloride was prepared from tribenzylarsine and benzyl chloride at 170—175°. The following double salts derived from tetrabenzylarsonium hydroxide were prepared: the *compound* $As(C_7H_7)_4I,HgI_2$ forms crystals melting at 163°; the *compound* $As(C_7H_7)_4Cl,HgCl_2$ crystallises in needles melting at 176°; the *platinichloride*, $[As(C_7H_7)_4Cl]_2PtCl_4$, melts at 198°; the *aurichloride*, $As(C_7H_7)_4Cl,AuCl_3$, crystallises in yellow needles melting at about 130°.

The double salts just described are identical with those obtained from mercury arsenide and alkyl iodides. K. J. P. O.

Organo-metallic Compounds. IWAN SHUKOFF (*Ber.*, 1905, 38, 2691—2693).—Tinmethyl bromide (Pfeiffer and Lehnardt, Abstr., 1903, i, 470) has the molecular electrical conductivities $\mu = 700—866$ in aqueous solutions with $v = 10—640$. This salt is therefore strongly hydrolytically dissociated in solutions of all strengths. Thalliumdiethyl chloride (Meyer and Bertheim, Abstr., 1904, i, 656) is a strong electrolyte, but is hydrolytically dissociated in highly dilute solutions. It has the molecular conductivities $\mu = 84—149$ in aqueous solutions with $v = 20—2560$ at 25°. When thalliumdiethyl chloride is electrolysed between platinum electrodes, crystalline metallic thallium and a gas consisting to the extent of 15 per cent. of unsaturated hydrocarbons are liberated at the cathode. The concentration of the thallium ions in the thalliumdiethyl chloride solution was determined by measuring the *E.M.F.* of a thallium electrode by the method of compensation:

$0{\cdot}05N$ $TlEt_2Cl$ – Normal electrode – $0{\cdot}750V$
$0{\cdot}05N$ $TlEt_2Cl$ – $0{\cdot}005N$ $TlEt_2Cl$ – $0{\cdot}029V$
$0{\cdot}005N$ $TlEt_2Cl$ – $0{\cdot}0005N$ $TlEt_2Cl$ – $0{\cdot}001V$
$0{\cdot}05N$ $TlEt_2Cl$ – $0{\cdot}0005N$ $TlEt_2Cl$ – $0{\cdot}030V$

The influence of dilution is less than that required by Nernst's formula, which appears to be characteristic for thallium salts. Measurements of the *E.M.F.* in thalliumdiethyl chloride solution against a thallium chloride solution saturated at 25° gave the following results:

$0{\cdot}0161N\ TlEt_2Cl$ – $0{\cdot}0161N\ TlCl$ – $0{\cdot}042V$
$0{\cdot}0161N\ TlEt_2Cl$ – Normal electrode – $0{\cdot}769V$
$0{\cdot}0161N\ TlCl$ – Normal electrode – $0{\cdot}727V$

Applying Nernst's formula to these results, the concentration of the thallium ions in thallium chloride solution is found to be $10^{-2{\cdot}07}$ whilst that in thalliumdiethyl chloride is $10^{-2{\cdot}78}$. The thalliumdiethyl cation is dissociated therefore to the extent of about 1/300 of its concentration. G. Y.

Cyclic Compounds. Heptanaphthene (Methyl*cyclo*hexane) and its Derivatives. WLADIMIR B. MARKOWNIKOFF (*Annalen*, 1905, **341**, 118—150. Compare Abstr., 1903, i, 19, 157; 1904, i, 383).—Heptanaphthene from naphtha has been compared with that prepared synthetically from the iodide of methyl*cyclo*hexanol by reduction with the zinc-copper or the zinc-platinum couple, and purified by treatment with potassium permanganate, nitric and sulphuric acids, sodium, and finally concentrated sulphuric acid. The hydrocarbon boils at 28° under 60 mm. and at 100·2° under 751 mm. pressure; its sp. gr. is 0·7859 at 0°/0°, 0·7697 at 20°/0°, and 0·774 at 15°/15°; it melts at – 147·5°. It reacts with bromine in the presence of aluminium bromide forming pentabromotoluene. It is not attacked by nitric and sulphuric acids at 80°, but is oxidised by fuming nitric acid with the formation of succinic acid. Sulphuric acid is without effect, but fuming sulphuric acid oxidises it. Iodine, bromine, and hydriodic acid have little action, whilst potassium permanganate oxidises the hydrocarbon slowly. It was found that the heptanaphthene could not be obtained pure from naphtha.

3-*Chloro*-1-*methyl*cyclo*hexane*, prepared from pure 1-methyl*cyclo*hexanol-3 and fuming hydrochloric acid, boils with decomposition at 63·5—65° under 40 mm. pressure, and has a sp. gr. 0·9664 at 20°/0° and 0·9844 at 0°/0°. The product consists of two stereoisomeric chlorides, of which one is unstable; the chief fraction boils at 69—70° under 40 mm. pressure, and has a sp. gr. 0·98487 at 0°/0°. The stable chloride boils at 160—161° under 756 mm. pressure. The tertiary chloride (1-*chloro*-1-*methyl*cyclo*hexane*) can be prepared from the corresponding tertiary alcohol (Abstr., 1900, i, 578); it boils at 53—55° under 40 mm. pressure and at 148—151° with decomposition under 752 mm. pressure. The same chloride is obtained by the action of chlorine on heptanaphthene, together with a second *chloride* which boils at 155·5—157·7° under 740 mm. pressure, and has a sp. gr. 0·960 at 15°/15°. A mixture of two bromides is formed when hydrobromic acid acts either on methyl*cyclo*hexanol or on naphthylene; one of these compounds is decomposed on distillation. The stable *bromide* boils at 181—181·2° under 758 mm. pressure and has a sp. gr. 1·268 at 15°/15°. The corresponding *iodide*, which also exists in two

isomeric forms, boils at 107° under 40 mm. and at 101—102° under 30 mm. pressure, and has a sp. gr. of 1·523 at 15°/15°; the same iodide is formed by the action of hydriodic acid on naphthaheptanaphthene chloride. The proof of the constitution of these monohalogen derivatives will be given in a subsequent communication.

K. J. P. O.

Electrolytic Oxidation of Hydrocarbons of the Benzene Series. Part II. Ethylbenzene, Cumene, and Cymene. HERBERT DRAKE LAW and F. MOLLWO PERKIN (*Trans. Faraday Soc.*, 1905, 1, 251—261).—The chief product obtained by the oxidation of ethylbenzene in sulphuric acid solution containing acetone, using a current density at the anode of 1·3 amperes per. sq. dcm., was phenylmethylcarbinol; phenylethyl alcohol was also found in small quantity and benzaldehyde made its appearance when the number of ampere hours was more than sufficient to oxidise the whole of the hydrocarbon to alcohol. When oxidised under the same conditions, cymene gave rise to cuminaldehyde and a mixture of mono- and di-hydric alcohols. The carbazone derived from the aldehyde was prepared; it crystallises in pearly plates melting and decomposing at 206—208°. When cumene boiling at 155—158° was oxidised with an anode density of 1·66 amperes per sq. dcm., a mixture of cuminaldehyde and hydratropaldehyde, and a mono- and a di-hydric alcohol was obtained.

These experiments confirm the results of earlier experiments carried out with toluene and the xylenes, and indicate that certain groups, for example, the aldehyde group, are relatively stable when acted on electrolytically. The protective action exerted by a negative group is illustrated by the oxidation of cymene, the *iso*propyl group not being attacked to any appreciable extent until the methyl group has been completely converted into the aldehyde group. The conclusion is drawn that the active oxidising agent in the electrolysis of dilute acid and alkaline solutions is the hydroxyl group and not oxygen. Even in acid solution, in consequence of the greater mobility of the hydroxyl ions, there is a tendency for these to concentrate around the anode.

Attempts to obtain phenose, $C_6H_6(OH)_6$, by electrolysing a mixture of benzene, sulphuric acid, and alcohol were unsuccessful. H. M. D.

Replacement of Atoms or Groups of Atoms by Hydrogen in Aromatic Compounds during Reduction. JAN J. BLANKSMA (*Rec. Trav. chim.*, 1905, [ii], 24, 320—326. Compare Loring Jackson, Abstr., 1896, i, 538).—On reduction with tin and hydrochloric acid in alcoholic solution, 1-iodo-2 : 4-dinitrobenzene, like the corresponding bromo-derivative (compare Zincke and Sintenis, Abstr., 1873, 167), yields *m*-phenylenediamine; 2 : 4-dinitrobenzenesulphonic acid, like the corresponding benzoic acid (compare Wurster, *Ber.*, 1874, **7**, 214), also yields *m*-phenylenediamine on reduction. 2 : 4 : 6-Tribromo-*m*-toluidine, when reduced by tin and hydrochloric acid, yields *m*-toluidine, and 2 : 4 : 6-tribromo-3 : 5-dinitrotoluene similarly yields *s*-tolylenediamine (compare Davis, Trans., 1902, **81**, 870). 3 : 5-Dibromo-?-dinitrotoluene, melting at 157° (compare Neville and Winther, Trans., 1881, **39**, 83),

yields, on reduction with tin and hydrochloric acid, 2 : 4-diaminotoluene whence it follows that the original compound is 3 : 5-dibromo-2 : 4-dinitrotoluene. Nitro-*p*-xylidinesulphonic acid (compare this vol., i, 426) is reduced by tin and hydrochloric acid to 3 : 5-diamino-*p*-xylene (compare this vol., i, 431). The author therefore draws the conclusion that when an aromatic compound containing a NH_2 group in the ortho- or para-position to the atom or group of atoms (Br, I, CO_2H, SO_3H) is reduced by tin and hydrochloric acid, the latter group is replaced by hydrogen, and this replacement is facilitated by the presence of the group OH, NH_2, or CH_3 in the meta-position to the NH_2 group. M. A. W.

Nitrating Action of Nitric Acid on Saturated Hydrocarbons. IX. Nitration of *o*-Xylene and its Products. Michael I. Konowaloff (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 530—537. Compare Abstr., 1903, i, 269).—*o*-Xylene is slowly attacked in open vessels by nitric acid of sp. gr. 1·075 and more readily by acid of sp. gr. 1·10. Under the same conditions, *p*-xylene is attacked more readily and *m*-xylene with more difficulty. This behaviour leads to a modification of Fittig and Velguth's method for purifying *m*-xylene (*Annalen*, 1868, **148**, 10), which is best carried out by boiling and constantly stirring the xylene with nitric acid of sp. gr. 1·075, the concentration being kept constant by the addition of acid; the nitro-compounds are subsequently removed by treating the mass with aqueous potassium hydroxide.

When heated in sealed tubes at 110° with nitric acid of sp. gr. 1·075, *o*-xylene yields *o*-tolylnitromethane, which crystallises in needles melting at 12—14°, boils at 145—146° under 23 mm. pressure, and has the sp. gr. 1·1572 at 0°/0° and 1·1423 at 18°/0° and n_D 1·54387 at 18°. *o*-Tolylnitromethane has been prepared by Goldberg (Abstr., 1901, i, 32) and by Wislicenus and Wren (this vol., i, 284), whose divergent results are ascribed by the author to the impurity of their material. When kept, *o*-tolylnitromethane becomes red and deposits a crystalline substance which contains more nitrogen than the original compound and melts at 238—242°. The *potassium* derivative of *o*-tolylnitromethane, $C_8H_8K\cdot NO_2$, forms shining scales, and its aqueous solution gives the following reactions: with copper sulphate, a dark green precipitate, soluble in ether or benzene, forming a red solution; with silver nitrate, a yellow precipitate, soluble in benzene with a dark red coloration; with mercuric chloride or stannic chloride, a white precipitate. The action of concentrated nitric acid of sp. gr. 1·5 effects substitution in the benzene nucleus of *o*-tolylnitromethane. The latter is reduced by tin and hydrochloric acid, giving the amine, $C_6H_4Me\cdot CH_2\cdot NH_2$, melting below 0° and boiling at 205·5—206° under 745 mm. pressure, and having the sp. gr. 0·9921 at 0°/0°, 0·9776 at 18°/0°, and 0·9768 at 19°/0°, and n_D 1·54356 at 19°; the hydrochloride melts at 219—220°, the platinichloride, with decomposition, at 220—223°, the hydrobromide at about 209°, the sulphate at 176—179°, the nitrate at 130°, the oxalate at 94—98°, the picrate at 214—215·5°, and the aurichloride at about 180°. T. H. P.

Nitrating Action of Nitric Acid on Saturated Hydrocarbons. X. Nitration in Acetic Acid Solution. Michael I. Konowaloff and Ch. Gurewitsch (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 537—542).—The authors give, in tabular form, the results of the nitration, in presence of acetic acid, of toluene, *o*-, *m*-, and *p*-xylenes, *ψ*-cumene, ethylbenzene, diethylbenzene, and *tert.*-butylbenzene, from which they arrive at the following conclusions: (1) the reactivity of aromatic hydrocarbons with a mixture of nitric and acetic acids obeys the rules already given by Konowaloff (Abstr., 1894, i, 265) for aqueous nitric acid. *tert.*-Butylbenzene is most difficult of attack, and then follow *o*- and *p*-xylene, *ψ*-cumene, ethylbenzene, and diethylbenzene. (2) Like water, acetic acid weakens the action of nitric acid on the aromatic nucleus and, especially on heating, directs the attack to the side-chain. (3) The latter is not only nitrated, but also oxidised, especially when the action of the nitric acid is energetic; acids are then obtained principally. (4) By suitable adjustment of the proportions of nitric and acetic acids, good yields of nitro-compounds substituted in the side-chain can be obtained, and this mixture of acids is sometimes to be preferred to aqueous nitric acid. (5) By using nitric acid, rendered moderately dilute by means of acetic acid, mononitro-compounds substituted in the nucleus can be obtained in cases where concentrated nitric acid acts too energetically. T. H. P.

Diphenylpropanes, especially *αα*-Diphenylpropane. Michael I. Konowaloff and S. Dobrowolsky (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 547—551).—*αα-Diphenylpropane*, $CHPh_2\cdot CH_2Me$, obtained by heating together diphenylethylcarbinol and hydriodic acid of sp. gr. 1·9 in a sealed tube at 140—150°, is a colourless liquid with a blue fluorescence, boils at 278·5—280° under 754 mm. pressure, and has the sp. gr. 0·9938 at 18·5°/0° and n_D 1·56809 at 18·5°.

αβ-Diphenylpropane, prepared by the condensation of allyl chloride and benzene in presence of aluminium chloride, boils at 280—281° under 758 mm. pressure and has sp. gr. 0·9809 at 23·5°/0° and n_D 1·5591 at 23·5°.

αγ-Diphenylpropane, prepared by condensing trichlorohydrin and benzene by means of aluminium chloride, boils at 298—299° and has the sp. gr. 1·0071 at 20°/0° and n_D 1·5760 at 20°. T. H. P.

Nitrating Action of Nitric Acid on Saturated Hydrocarbons. XI. Non-nuclear Nitration of Homologues of Diphenylmethane. Michael I. Konowaloff and M. G. Jatzewitsch (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 542—547. Compare preceding abstract; Abstr., 1894, i, 265; 1895, i, 633; Anschütz and Romig, Abstr., 1885, 768; 1886, 1033).—On heating pure diphenylethane with nitric acid of sp. gr. 1·075, it yields: (1) an oil; (2) a *substance*, $C_{14}H_{13}O_3N$, which separates from acetic acid in colourless, prismatic crystals, or from light petroleum in slender needles melting at 107—108°, and dissolves readily in ether and to a less extent in alcohol; when treated with sodium ethoxide, it gives benzophenone, but with ferric chloride it does not give the reaction for nitro-compounds; on reduction with zinc dust and acetic acid, it yields a *base*,

$OH \cdot C_2H_2Ph_2 \cdot NH_2$, which forms white crystals melting at 107—108° and gives a *platinichloride*, $(C_{14}H_{15}ON)_2,H_2PtCl_6,3H_2O$, melting at 146—149°. On treatment with acetyl chloride, the substance (2) is converted into a yellow, crystalline compound (No. 2 of Anschütz and Romig) which melts at 87—88°, seems to be saturated, and gives with ferric chloride the reaction for nitro-compounds; on reduction with zinc dust and acetic acid, it yields a syrupy *base*, the hydrochloride of which melts at 170—173°. The action of sodium ethoxide on the yellow compound melting at 87—88° or on the oily product (1) gives the sodium derivative of *α-nitro-β-ethoxy-ββ-diphenylethane*,

$$NO_2 \cdot CH_2 \cdot CPh_2 \cdot OEt,$$

which separates from a mixture of ether and light petroleum in large, colourless crystals melting at 91—92° and dissolves readily in acetic acid and to a less extent in alcohol or benzene; by its behaviour towards ferric chloride and to Meyer's reaction, it is shown to be a primary nitro-compound; treatment with acetyl chloride gives the original compound melting at 87—88°, whilst reduction with zinc dust and acetic acid gives an amine, forming a crystalline *platinichloride*, $[OEt \cdot C_2H_2Ph_2 \cdot NH_2]_2,H_2PtCl_6,2H_2O$. The action of sodium amyloxide on the product melting at 87—88° yields a *compound* which melts at 95—97° and is different from α-nitro-β-ethoxy-ββ-diphenylethane.

Nitration of diphenylethane with a mixture of nitric and acetic acids yields the same products as are obtained by nitric acid of sp. gr. 1·075.

From the above results the authors draw the conclusion that the action on diphenylethane of nitric acid diluted with either water or acetic acid yields nitro-compounds with the nitro-groups in the side-chain.

T. H. P.

Nitrating Action of Nitric Acid on Saturated Hydrocarbons. XII. Nitration of Homologues of Diphenylmethane in the Side-chain. MICHAEL I. KONOWALOFF and S. DOBROWOLSKY (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 551—555).—The authors have studied the nitration of αα-, αβ-, and αγ-diphenylpropanes when heated in open vessels with nitric acid of sp. gr. 1·075.

αγ-Diphenylpropane yields primary and secondary nitro-products, the former being probably formed from an isomeric diphenylpropane present as an impurity.

αβ-Diphenylpropane gives (1) *γ-nitro-αβ-diphenylpropane*,

$$CH_2Ph \cdot CHPh \cdot CH_2 \cdot NO_2,$$

which forms prisms melting at 153—155° and dissolves readily in benzene, alcohol, or acetone, and to a less extent in ether; (2) a tertiary nitro-compound, yielding on reduction an amine, the *hydrochloride* of which, $C_3H_5Ph_2 \cdot NH_2,HCl$, melts at 177—178° and the *platinichloride* at 180°.

αα-Diphenylpropane gives products similar to those obtained from the analogous diphenylethane (compare Konowaloff and Jatzewitsch, preceding abstract). The heavy yellow oil obtained gives, with sodium ethoxide, the sodium salt of β-nitro-α-ethoxy-αα-diphenylpropane (?),

$OEt\cdot CPh_2\cdot CHMe\cdot NO_2$, which crystallises from ether in yellow prisms melting at 103—104°, is readily soluble in alcohol or benzene, gives Meyer's reaction for secondary nitro-derivatives, and reacts with ferric chloride. There is also formed (1) a tertiary nitro-compound, which yields on reduction an amine, the hydrochloride of which melts at 206—208°, and (2) the *ethyl* derivative of *diphenylethylcarbinol*,

$$CPh_2Et\cdot OEt,$$

which melts at 160—161°. T. H. P.

Reduction of Nitro-compounds by Alcohols in presence of Alkali. TH. ROTARSKI (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 569—575).—The action of sodium alkyloxides on aromatic nitro-compounds proceeds in one of two ways: (1) at low temperatures,

$$2ArNO_2 + 3MeONa = \begin{matrix}ArN\\ |\\ ArN\end{matrix}\!>O + 3NaOH + 3H\cdot CHO;$$

(2) at high temperatures,

$$2ArNO_2 + 3MeONa = \begin{matrix}ArN\\ |\\ ArN\end{matrix}\!>O + 3H\cdot CO_2Na + 3H_2.$$

The author has investigated the reduction of nitrobenzene, *p*-nitroanisole, and *p*-nitrophenetole by various alcohols in presence of different alkalis. At low temperatures, the action is simply that of hydrogen, so that theoretically there should be formed all reduction products obtainable from either one or two molecules of the nitro-compound. At higher temperatures, the reducing action of alkyloxides consists only in taking oxygen away from the nitro-compound, so that in this case only compounds poorer in nitrogen can be obtained—azoxy-, azo-, and nitroso-compounds, and not compounds formed by the replacement of oxygen by hydrogen, namely, hydrazo- and amino-compounds, and arylhydroxylamines. In order to increase the yield of azoxy-derivative, which is the chief product of the reaction, the temperature at which the latter is carried out must be raised. The temperature above which one of these reactions and below which the other takes place varies with the nature both of the alcohol and of the nitro-compound and with the amount of alkali present.

The results obtained are summarised by the author as follows: the use of alkali and alcohol has no advantage over that of sodium alkyloxide for the reduction of nitro-compounds. Aldehydes do not reduce nitro-compounds, even in presence of alkali. The sodium alkyloxide may be replaced by barium oxide or hydroxide *plus* an alcohol, but lime, magnesium oxide, or alumina may not be used. If, at the high temperature used for the reduction of nitro-compound to azoxy-compound, the sodium alkyloxide causes decomposition, barium oxide or hydroxide may be employed with advantage. The alcohol used as a diluent with sodium alkyloxide may be replaced by other liquids, such as benzene or toluene. T. H. P.

***cyclo*Hexanesulphonic Acid.** WALTHER BORSCHE and W. LANGE (*Ber.*, 1905, **38**, 2766—2769).—*cyclo*-Hexyl chloride readily forms a Grignard compound with magnesium, and this with dry sulphur dioxide yields magnesium *cyclo*-hexanesulphinate, which is soluble

in water. When oxidised with a cold saturated solution of permanganate, the sulphinate yields dihexamethylene sulphone and *potassium* cyclo*hexanesulphonate*, $C_6H_{11}\cdot SO_2\cdot OK$. This is readily soluble in water and crystallises from alcohol in glistening plates. The *chloride*, $C_6H_{11}\cdot SO_2Cl$, is a colourless oil distilling at 127—128° under 15 mm. pressure, but decomposes when slowly distilled. The *acid* crystallises from alcohol and melts at 90—92°. The *anilide*, $C_6H_5\cdot SO_2\cdot NHPh$, crystallises from dilute alcohol in flat needles and melts at 87°. The *ethyl* ester, obtained by the action of sodium ethoxide on the chloride, is a colourless oil which distils at 150—151° under 18 mm. pressure. When reduced, the chloride yields cyclo*hexyl hydrosulphide*, $C_6H_{11}SH$.

*Di*cyclo*hexanesulphone*, $SO_2(C_6H_{11})_2$, is sparingly soluble in hot water and crystallises in colourless needles melting at 132—132·5°. Di*cyclo*hexyl (Abstr., 1902, i, 360) is obtained as a by-product in the preparation of magnesium *cyclo*hexanesulphinate. J. J. S.

Action of Pure [Absolute] Nitric Acid on Benzenesulphomethylamide. H. J. BACKER (*Rec. Trav. chim.*, 1905, [ii], **24**, 484—491).—When benzenesulphomethylamide is nitrated with fuming nitric acid, the product is benzenesulphomethylnitroamide (compare Van Romburgh, *Rec. Trav. chim.*, 1884, **3**, 7), but when pure (absolute) nitric acid is employed, the *m*-nitro-derivative of this compound is produced. m-*Nitrobenzenesulphomethylnitroamide*, $NO_2\cdot C_6H_4\cdot SO_2\cdot NMeNO_2$, can also be formed by the action of pure nitric acid on *m*-nitrobenzenesulphomethylamide (compare Chattaway, Trans., 1905, **87**, 159); it forms colourless needles melting at 96°, readily soluble in chloroform, benzene or acetone, warm alcohol, carbon disulphide, or ether, insoluble in light petroleum; on boiling with 10 per cent. potassium hydroxide solution, it yields potassium nitrobenzenesulphonate, from which *m*-nitrobenzenesulphonamide, m. p. 160·5—161° (compare Schober and Kiefer, Abstr., 1895, i, 52), is obtained, or the same compound can be prepared by the action of ammonia on the original nitroamide.

M. A. W.

Grignard's Reaction. ADOLF VON BAEYER (*Ber.*, 1905, **38**, 2759—2765).—Magnesium does not readily react with ethereal solutions of iodo-derivatives of aniline, but the metal may be rendered active by heating in a flask over a free flame and adding gradually about half its weight of iodine, the flask being continually rotated. After treatment in this way, the metal reacts to a slight extent with water, but very vigorously with methyl alcohol, with an ethereal solution of bromobenzene, or with iodo-derivatives of aniline or of dimethylaniline; the reaction is most vigorous with the ortho-compounds, and least with the para. The best method for preparing the magnesium derivatives is to add the active magnesium gradually to the dry ethereal solution of the iodo-derivative. Magnesium *o*-dimethylaminophenyl iodide and methyl dimethylanthranilate (Willstätter and Kahn, Abstr., 1904, i, 235) react yielding *tetramethyl*-2 : 2′-*diaminobenzophenone*, $C_{17}H_{20}ON_2$, which crystallises from light

petroleum in brilliant yellow prisms melting at 122°. The ethereal solutions of the magnesium iodo-derivatives from the iodo-anilines react readily with benzophenone, yielding aminotriphenylcarbinol derivatives. Magnesium *o*-aminophenyl iodide and methyl benzoate yield benzanilide.

Details for the preparation of the iodo-derivatives of aniline are given. The dimethyl derivatives were prepared by the action of methyl sulphate (Ullmann, Abstr., 1903, i, 394). *o*-Iodoaniline melts at 60—61°, *o*-iododimethylaniline boils at 116° under 11 mm. pressure; m-*iododimethylaniline* melts at 38—39° and distils at 142—143° under 12 mm. pressure. *p*-Iodoaniline melts at 67—68° and the dimethyl derivative at 82°. J. J. S.

α-Anthramine and α-Anthrol. Hans Dienel (*Ber.*, 1905, 38, 2862—2867. Compare Liebermann and Simon, Abstr., 1882, 857; Liebermann and Hoermann, *ibid.*, 858; Liebermann and Bollert, *ibid.*, 1105; Liebermann and Hagen, *ibid.*, 1212; Iljinsky, Abstr., 1904, i, 176; Schmidt, *ibid.*, 256).—Ammonio-zinc anthracene-1-sulphonate, $(C_{14}H_9SO_3)_2Zn,2NH_3,H_2O$, crystallises in needles from the ammoniacal mother liquors from the reduction of anthraquinone-1-sulphonate with zinc dust and ammonia; when treated with water, it decomposes with formation of zinc dust.

1-Anthrol, formed by fusing potassium anthracene-1-sulphonate with potassium hydroxide at 250—260°, crystallises in brown leaflets or needles, sinters at 146°, and melts and decomposes at 150—153°. It dissolves in the ordinary solvents more easily than does 2-anthrol, to form solutions with blue fluorescence; the solution in aqueous ammonia is green, in dilute alkali hydroxides or baryta yellow with green fluorescence; with traces of nitric acid, the solution in glacial acetic acid forms a dark red coloration, with ferric chloride a green precipitate. The *acetyl* derivative crystallises in colourless needles, becomes brown at about 80°, melts and decomposes at 128—130°, and is oxidised by chromic acid in hot acetic acid solution to erythro-1-acetoxyanthraquinone, $C_{14}H_{17}O_2\cdot OAc$, which crystallises in glistening, golden needles melting at 175—178°. The *ethyl ether*, $C_{16}H_{14}O$, formed by boiling 1-anthrol with alcoholic hydrogen chloride in a reflux apparatus, crystallises in colourless needles, melts at 69°, and dissolves in alcohol to form a solution with blue fluorescence; the *methyl ether* crystallises in colourless leaflets and melts at 70°. These ethers are formed more slowly and in poorer yields and melt at lower temperatures than the corresponding 2-compounds.

1-*Anthramine*, $C_{14}H_9\cdot NH_2$, formed by heating 1-anthrol with acetamide in a sealed tube at 260°, crystallises in glistening, yellow leaflets, melts at about 130°, is more soluble than the 2-amine, gives the same colour reactions with bromine and concentrated nitric acid, but a greyish-green coloration with arsenic acid, and has only weak basic properties. The *hydrochloride*, $C_{14}H_{11}N,HCl$, and the sulphate are white, crystalline substances. The *acetyl* derivative, $C_{14}H_{11}NAc$, crystallises in green needles, melts at 198°, and is oxidised to α-acetylaminoanthraquinone by chromic acid in glacial acetic acid solution.

Dihydro-1-*anthramine*, $C_6H_4<\substack{CH_2\\CH_2}>C_6H_3\cdot NH_2$, formed by reduction of 1-anthramine with sodium amalgam in boiling alcoholic solution, crystallises in slender, glistening, colourless needles, has an odour of dihydroanthracene, and sinters at 60—70°, but has no sharp melting point. The *hydrochloride*, $C_{14}H_{13}N,HCl$, forms glistening leaflets.

Di-1-*anthramine*, $NH(C_{14}H_9)_2$, is formed when 1-anthramine is boiled with glacial acetic acid in a reflux apparatus. It crystallises in glistening leaflets, melts at 204°, is insoluble in concentrated hydrochloric acid, and is less volatile and less soluble than 1-anthramine.

G. Y.

Bromine Additive Compounds of Dimethylaniline. C. LORING JACKSON and LATHAM CLARKE (*Amer. Chem. J.*, 1905, **34**, 261—290).—The following nomenclature is suggested for the compounds described in this paper. Additive compounds containing the bromine attached to a carbon atom of the benzene nucleus are termed benzbromides; if the bromine is united to the nitrogen, the compounds are amine dibromides (or hydrobromides); and when the additive bromine is attached to a bromine atom, the compounds are termed perbromides.

Fries (Abstr., 1904, i, 571) has already obtained certain bromine additive compounds of dimethylaniline by adding bromine to a solution of dimethylaniline or its hydrobromide in glacial acetic acid. The compounds now described were prepared by the addition of bromine to dimethylaniline dissolved in chloroform.

3 : 4-*Dibromodimethylaminodihydrobenzene* (benz-3 : 4-dibromide of dimethylaniline), $C_6H_5Br_2\cdot NMe_2$, crystallises in long, slightly yellow plates or slender needles, melts at about 82°, is soluble in alcohol, chloroform, or acetone, and on exposure to the air is slowly converted into *p*-bromodimethylaniline; it dissolves in dilute acids, does not liberate iodine from potassium iodide, and is turned reddish-brown by quinone. When this substance is treated with excess of ethyl bromide, the additive *compound* (benz-3 : 4-dibromide of dimethylethylphenylammonium bromide), $C_6H_5Br_2\cdot NMe_2EtBr$, is produced, which crystallises in flat, white prisms, and by the action of water is converted into a red oil.

3 : 4-*Dibromodimethylaminodihydrobenzene dibromide* (benz-3 : 4-dibromide of dimethylaniline dibromide), $C_6H_5Br_2\cdot NMe_2,Br_2$, crystallises in long, yellowish-red needles, melts at 65—70°, is soluble in alcohol, chloroform, acetone, or ethyl acetate, is insoluble in dilute acids, and is converted by potassium hydroxide into dibromodimethylaniline; it dissolves in ethyl bromide and crystallises unchanged from the solution, and gives a blue coloration with potassium iodide and starch paste. When this substance is treated with acetone, it is converted into 3 : 4-dibromodimethylaminodihydrobenzene, whilst by the action of alcohol the *hydrobromide* of dibromodimethylaniline is produced, which melts at 110°. When 3 : 4-dibromodimethylaminodihydrobenzene dibromide is moistened with chloroform, it gradually changes into a red *substance*, $C_{16}H_{24}N_2Br_7$, which contains one atom of bromine capable of replacing iodine in potassium iodide and melts at 105°;

it is not identical with the compound $(C_6H_3Br_2{\cdot}NMe_2,HBr)_2Br$, described by Fries (*loc. cit.*). By the action of hot chloroform on the dibromide, a viscous substance is produced which does not react with potassium iodide, is converted by sodium thiosulphate into dibromodimethylaniline, and is probably the compound $C_6H_4Br_3{\cdot}NMe_2,HBr$; if left for several days, it changes into a red compound similar to that already described, and becomes capable of liberating iodine from potassium iodide.

Tetrabromodimethylaminotetrahydrobenzene dibromide (benztetrabromide of dimethylaniline dibromide), $C_6H_5Br_4{\cdot}NMe_2,Br_2$, crystallises in small, red needles and is very unstable; it readily loses hydrogen bromide, becoming converted into *tribromodimethylaminodihydrobenzene dibromide* (benzdibromide of bromodimethylaniline dibromide),

$$C_6H_4Br_3{\cdot}NMe_2,Br_2,$$

which forms long, red prisms, melts at 78°, and is converted by potassium hydroxide into dibromodimethylaniline. By the action of acetone on the compound last described, an oily *substance* is formed which does not react with potassium iodide and is probably the benzdibromide of bromodimethylaniline, $C_6H_4Br_3{\cdot}NMe_2$. When the compound containing five bromine atoms is treated with alcohol, it is converted into a substance which is probably identical with the *o-p*-dibromodimethylaniline hydrobromide perbromide described by Fries (*loc. cit.*). The compound reacts with aniline with formation of aniline hydrobromide, dibromodimethylaniline, and small quantities of a *substance* which forms red crystals, whilst when treated with a mixture of potassium iodide and sodium thiosulphate it is converted into *p*-bromodimethylaniline. If a solution of the substance in chloroform is treated with solid potassium iodide, the *compound*

$$C_6H_3Br_2{\cdot}NMe_2,HBr,I$$

is formed, which crystallises in reddish-yellow prisms and melts at 137°. By the action of sodium acetate on the benzdibromide of dimethyl-*p*-bromoaniline dibromide, dibromodimethylaniline is produced.

When bromine is added to a chloroform solution of *p*-bromodimethylaniline, the compound $C_6H_3Br_2{\cdot}NMe_2,HBr,Br_2$ (Fries, *loc. cit.*) is obtained. By the action of bromine on dibromodimethylaniline, the *perbromide*, $C_6H_3Br_2{\cdot}NMe_2,HBr_4$, is formed, which crystallises in yellowish-red, flat prisms, melts at 98°, is converted by acetone into the hydrobromide of dibromodimethylaniline, by potassium hydroxide into dibromodimethylaniline, by cold alcohol into the perbromide,

$$(C_6H_3Br_2{\cdot}NMe_2,HBr)_2Br$$

(Fries, *loc. cit.*), and by hot alcohol or chloroform into *tribromodimethylaniline hydrobromide*, which darkens at 200° and melts at 202°.

p-*Bromodimethylaniline di-iodide*, $C_6H_4Br{\cdot}NMe_2,I_2$, obtained by the action of iodine on a chloroform solution of *p*-bromodimethylaniline, crystallises in flat, black prisms, melts at 115°, and is slightly soluble in alcohol, acetone, or ethyl acetate. E. G.

ω-Sulphomethyl Derivatives of Aromatic Amines. Badische Anilin- & Soda-Fabrik (D.R.-P. 158718. Compare this vol., i, 340).—Diphenylamine reacts with formaldehyde and sodium hydro-

gen sulphite: $CH_2(NPh_2)_2 + HSO_3Na = NPh_2{\cdot}CH_2{\cdot}SO_3Na + NHPh_2$. The *sodium* salt thus obtained separates in glistening, colourless needles. Potassium chloride precipitates the sparingly soluble *potassium* salt. The *ω-sulphonic acid* is stable, and reacts with metallic cyanides to form the viscous *nitrile*. C. H. D.

Preparation of α-Phenyl- and *p*-Tolyl-naphthylamine-6- and -7-sulphonic Acids. Aktien-Gesellschaft für Anilin-Fabrikation (D.R.-P. 159353).—In addition to α-naphthylamine-4 : 8-disulphonic acid (this vol., i, 717), α-naphthylamine-4 : 6- and -4 : 7-disulphonic acids also lose the 4-sulphonic group when heated with aniline or *p*-toluidine at 180°, arylation of the amino-group taking place at the same time, yielding *α-phenyl-* or *α-p-tolyl-naphthylamine-6-* or *-7-sulphonic acid*. C. H. D.

Action of Formaldehyde on Thiocarbanilide. Erich Oppermann (*Chem. Zeit.*, 1905, 29, 1075—1076).—A mixture of finely-powdered thiocarbanilide with formaldehyde was treated with dry hydrogen chloride until all the thiocarbanilide had dissolved; the substance obtained, on treatment with excess of ice-cold water, gave a white, flocculent precipitate which could not be purified; the acid filtrate from the latter, when made alkaline with sodium hydroxide, deposited a substance which crystallised from alcohol in groups of needles melting at 78°, and was readily soluble in cold benzene, ether, acetone, or chloroform; it was decomposed by solution in hot 30 per cent. sulphuric acid. Molecular weight determinations gave the values 239 and 246, and these, combined with the analytical results, lead to the formula $NPh{:}C{<}\begin{matrix}S\text{——}CH_2\\NPh{\cdot}CH_2\end{matrix}{>}O$. The corresponding derivatives obtained from π-chloro- and π-bromo-thiocarbanilide melt at 84° and 80° respectively. The former crystallises from alcohol in small, white plates, and the latter in white, transparent plates. P. H.

Preparation of β-Arylhydroxylamines by the Electrochemical Reduction of Aromatic Nitro-compounds. Kurt Brand (*Ber.*, 1905, 38, 3076—3078).—A fine suspension of nitrobenzene in an aqueous solution of acetic acid and sodium acetate is placed in a porous pot, which serves as the cathode vessel and is kept automatically stirred. The pot is surrounded by a lead pipe which serves as anode and through which cold water is passed, so that the temperature is kept at 20—25°. The whole is placed in a glass vessel containing dilute sulphuric acid. The cathode is a nickel wire gauze of 3—4 sq. cm. surface, and a voltage of 6—8 with a current of 6—10 amperes yields the best results. From 50 grams of nitrobenzene 32 grams of phenylhydroxylamine have been obtained, together with a trace of azoxybenzene and a little aniline.

p-Chlorophenylhydroxylamine has been prepared in a similar manner using an alcoholic solution of the nitro-compound mixed with an aqueous solution of acetic acid and sodium acetate. J. J. S.

Action of Phenylcarbimide on Sulphonic Acids. C. VALLÉE (*Bull. Soc. chim.*, 1905, [iii], **33**, 966—969).—Haller has shown that organic acids react with phenylcarbimide to form diphenylcarbamide and the anilide of the acid. It is now found that sulphonic acids and phenylcarbimide form principally the aniline sulphonates, with little diphenylcarbamide and no anilide.

A comparison of the products obtained by the interaction of phenylcarbamide and acetic and chloro-, dichloro-, and trichloroacetic acids in *N*-aqueous solution with those obtained with benzenesulphonic acid in *N*/2·4 solution shows that the amount of aniline salt formed increases, whilst that of the diphenylcarbamide decreases, with increasing affinity of the acid.

	Affinity, HCl = 100.	Of 100 grams of phenylcarbimide, there were recovered from the product as Aniline salt.	Anilide.	Diphenylcarbamide.
Acetic acid, *N*	0·4	5·58	0·0	94·41
Chloroacetic acid	4·8	20·00	4·66	75·33
Dichloroacetic acid	27·0	30·16	14·11	58·41
Trichloroacetic acid	75·0	51·83	traces	48·16
Benzenesulphonic acid, *N*/2·4	104·0	91·66	0·0	8·33

These results are due to the varying ionisation of the acids, as is shown by the formation of the anilide only without any aniline salt by the action of phenylcarbimide on trichloroacetic acid in *N*-toluene solution. G. Y.

Action of Aromatic Aldehydes on Sodium 1-Methyl-3-*cyclo*hexanoxide. ALBIN HALLER and FRANÇOIS MARCH (*Bull. Soc. chim.*, 1905, [iii], **33**, 969—974. Compare this vol., i, 276; Haller, Abstr., 1900, i, 301; Martini, Abstr., 1904, i, 903).—The action of 1 mol. of sodium 1-methyl-3-*cyclo*hexanoxide in toluene solution on more than 2 mols. of benzaldehyde, cooled by ice, leads to the formation of 4-hydroxybenzyl-1-methyl-3-*cyclo*hexanol (Tetry, Abstr., 1902, i, 469), benzyl alcohol, dibenzylidene-1-methyl-3-*cyclo*hexanol, melting at 127°, and 1-*methyl*-3-cyclo*hexanyl benzoate*, $C_{14}H_{18}O_2$, which melts at 66—67° and is easily soluble in ether, alcohol, or light petroleum. This may be formed also by the action of benzoyl chloride on sodium methyl*cyclo*hexanoxide or on methyl*cyclo*hexanol in presence of piperidine. The action of 1 mol. of sodium 1-methyl-3-*cyclo*hexanoxide on 1 mol. of benzaldehyde in toluene solution, the mixture being heated to complete the reaction, leads to the formation of 4-benzyl-1-methyl-3-*cyclo*hexanol and a small amount of sodium benzoate.

Similarly, the action of 1 mol. of sodium 1-methyl-3-*cyclo*hexanoxide on 2 mols. of anisaldehyde in the cold leads to the formation of anisyl alcohol and 4-anisylidene-1-methyl-3-*cyclo*hexanone, but on 1 mol. of anisaldehyde, and with heating to complete the reaction, to the formation of anisic acid and 4-*anisyl*-1-*methyl*-3-cyclo*hexanol*,

$$CHMe{<}\begin{matrix}CH_2\cdot CH(OH)\\ CH_2 \text{———} CH_2\end{matrix}{>}CH\cdot CH_2\cdot C_6H_4\cdot OMe.$$

This is obtained as a white powder, melts at 93—94°, and has $[\alpha]_D + 6°30'$ in alcoholic solution.

4-*Anisyl*-1-*methyl*-3-cyclo*hexanone*, $C_{15}H_{20}O_2$, formed by reduction of the anisylidene compound with sodium amalgam in presence of alcohol, melts at 52—53°, and on reduction with sodium and alcohol yields anisylmethyl*cyclo*hexanol. G. Y.

*cyclo*Butyldimethylcarbinol and its Transformations. Nic. M. Kijner (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 509—517).—cyclo-*Butyldimethylcarbinol*, $CH_2{<}^{CH_2}_{CH_2}{>}CH{\cdot}CMe_2{\cdot}OH$, prepared by Masson's method (Abstr., 1901, i, 249) by the action of magnesium methiodide on ethyl *cyclo*butanecarboxylate, is a mobile liquid with an odour resembling that of camphor, and boils at 147°, has the sp. gr. 0·8952 at 20°/0°, and n_D 1·4457 at 20°. The action of hydrogen bromide on the alcohol yields two bromides: (1) one, which was not isolated, giving, under the action of alcoholic potassium hydroxide, a *hydrocarbon*, $CH_2{<}^{CH_2}_{CH_2}{>}C{:}CMe_2$, boiling at 100—102° under 753 mm. pressure, and having the sp. gr. 0·7852 at 20°/0° and n_D 1·4371 at 20°; (2) the *bromide*, $CH_2{<}^{CH_2}_{CH_2}{>}CH{\cdot}CMe_2Br$, which is a colourless liquid turning yellow, and later dark green, when kept, and which boils at 167° under 755 mm. pressure, has the sp. gr. 1·2562 at 20°/0° and n_D 1 4796 at 20°; when reduced by means of the copper-zinc couple in alcohol, it yields a hydrocarbon which is probably 1 : 1-*dimethyl*cyclo*pentane*, $CMe_2{<}^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}$, and boils at 88·3—88·5° under 756 mm. pressure, and has sp. gr. 0·7553 at 20°/0° and n_D 1·4132 at 20°. On heating with hydriodic acid at 225°, *cyclo*butyldimethylcarbinol yields 1 : 3-dimethyl*cyclo*pentane. T. H. P.

*cyclo*Butyldiethylcarbinol and its Compounds. Nic. M. Kijner and W. Amosoff (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 517—520).—cyclo*Butyldiethylcarbinol*, $CH_2{<}^{CH_2}_{CH_2}{>}CH{\cdot}CEt_2{\cdot}OH$, prepared by Masson's method (Abstr., 1901, i, 249) by the action of magnesium ethiodide on ethyl tetramethylenecarboxylate, is a viscous liquid boiling at 188—189° under 759 mm. pressure, and having the sp. gr. 0·9176 at 0°/4° and 0·9010 at 20°/4° and n_D 1·4554 at 20°.

When distilled with oxalic acid, it gives the *hydrocarbon*,

$$CH_2{<}^{CH_2}_{CH_2}{>}C{:}CEt_2,$$

which has sp. gr. 0·8092 at 20°/0° and n_D 1·4510 at 20°. When shaken with concentrated sulphuric acid, this compound passes into cyclo*butyldiethylmethane*, $CH_2{<}^{CH_2}_{CH_2}{>}CH{\cdot}CHEt_2$, which boils at 151—152° under 775 mm. pressure and has sp. gr. 0·7946 at 19°/0° and n_D 1·4334 at 20°.

Reduction of *cyclo*butyldiethylcarbinol by means of hydriodic acid gives a *hydrocarbon*, C_9H_{18}, which boils at 148—149° under 767 mm. pressure, and has sp. gr. 0·7851 at 20°/0° and n_D 1·4298 at 20°.

T. H. P.

Triphenylcarbinols. Hugo Kauffmann and Ad. Grombach (*Ber.*, 1905, **38**, 2702—2706. Compare this vol., i, 280; Gomberg, Abstr., 1902, i, 534).—When boiled with alcoholic zinc chloride (compare Ullmann and Mourawiew-Winigradoff, this vol., i, 642), diphenyl-2 : 5-dimethoxyphenylcarbinol yields *diphenyl*-2 : 5-*dimethoxyphenylmethane*, $C_{21}H_{20}O_2$, which crystallises in white needles, melts at 104°, and gives a yellow coloration with concentrated sulphuric acid. With this acid, the carbinol gives an emerald-green coloration. If the carbinol is boiled for more than a few minutes with alcoholic zinc chloride, in the place of the methane there are obtained a liquid *product* which has an odour resembling that of safrole and is volatile in a current of steam, and a solid *substance*, which melts at 192° and is only slightly soluble in alcohol.

Diphenyl-2 : 5-*dimethoxyphenylmethyl chloride*, $C_6H_3(OMe)_2\cdot CPh_2Cl$, is formed when a current of hydrogen chloride is passed through a benzene solution of the carbinol containing anhydrous sodium sulphate, and the green solution so obtained is distilled finally in a vacuum. It crystallises from light petroleum in white needles, melts at 98°, reacts easily with traces of moisture, and when boiled with alcohol is reduced to diphenyl-2 : 5-dimethoxyphenylmethane. This is formed directly by the action of hydrogen chloride on the carbinol covered with warm alcohol; if the green alcoholic solution so formed is concentrated too far, a *second* modification of diphenyl-2 : 5-dimethoxyphenylmethane separates on cooling as an oil. This solidifies to crystals which melt and change into the first modification at 84°. The more fusible form is produced also from the less fusible by crystallisation from a super-cooled, highly concentrated alcoholic solution.

In the formation of the methane from the carbinol or its chloride, in presence of alcohol, the latter is oxidised to acetaldehyde.

Diphenyl-2 : 5-dimethoxyphenylmethane, melting at 104°, is obtained also when the carbinol is reduced by zinc dust in boiling glacial acetic acid solution. When heated with alcoholic zinc dust, triphenylcarbinol yields triphenylmethane. G. Y.

Action of Potassium Hydroxide on Mixtures of Ketones with Phenylacetylene. Alexei E. Faworsky (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 643—645).—The action of anhydrous potassium hydroxide on a mixture of a ketone with phenylacetylene yields an unsaturated alcohol, the reaction taking place in two stages: the potassium hydroxide is first added to the carbonyl group of the ketone, $>C{:}O + KOH = >C(OH)\cdot OK$, the latter then gradually reacting with the phenylacetylene according to the equation $>C(OH)\cdot OK + CH{:}CPh = >C(OH)\cdot C{:}CPh + KOH$. The reaction is hence similar to that occurring between potassium hydroxide, a ketone, and chloroform, which also takes place in two stages, the group $>C(OH)\cdot OK$, formed in the first, reacting with the chloroform, thus: $>C(OH)\cdot OK + CHCl_3 = >C(OH)\cdot CCl_3 + KOH$. In this case, however, the yields obtained are not so good as in the above synthesis of unsaturated alcohols, in which water can be almost completely excluded. T. H. P.

Action of Potassium Hydroxide on a Mixture of Phenylacetylene and Acetone: Synthesis of Phenylacetylenyldimethylcarbinol. M. SKOSSAREWSKY (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 645—647).—*Phenylacetylenyldimethylcarbinol*,

$OH\cdot CMe_2\cdot C⋮CPh$,

prepared by gradually adding finely-powdered potassium hydroxide to a mixture of phenylacetylene (1 mol.) and acetone (1 mol.) diluted with an equal volume of ether and cooled to 0°, separates from ether in colourless crystals melting at 53°. It forms an *acetyl* derivative, $C_{13}H_{14}O_2$, boiling at 130—135° under 10 mm. pressure. When heated with 5 per cent. sulphuric acid solution, the alcohol yields a *hydrocarbon*, $CH_2:CMe\cdot C⋮CPh$, boiling at 88° under 7 mm. pressure. When boiled with aqueous potassium hydroxide, phenylacetylenyldimethylcarbinol yields acetone and phenylacetylene. T. H. P.

Action of Potassium Hydroxide on a Mixture of Phenylacetylene with Methyl Ethyl Ketone: Synthesis of Phenylacetylenylmethylethylcarbinol. IWAN BORK (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 647—650. Compare preceding two abstracts).—*Phenylacetylenylmethylethylcarbinol*, $OH\cdot CMeEt\cdot C⋮CPh$, prepared by the interaction of potassium hydroxide, methyl ethyl ketone, and phenylacetylene, is a syrupy liquid with a pleasant odour recalling that of rose-oil; it boils at 129—130° under 9 mm. pressure, and has the sp. gr. 1·0039 at 0°/0° and 0·9906 at 20°/20°. On boiling with 10 per cent. potassium hydroxide solution, it is resolved into methyl ethyl ketone and phenylacetylene. When boiled with 5 per cent. sulphuric acid solution, it yields the *hydrocarbon*, $CHMe:CMe\cdot C⋮CPh$, as a liquid which has a smell resembling that of honey, boils at 102—103° under 9 mm. pressure, and has the sp. gr. 0·9462 at 0°/0° and 0·9305 at 20°/20°; on treatment with concentrated sulphuric acid at the ordinary temperature and then with water, the hydrocarbon undergoes hydration to phenylacetylenylmethylethylcarbinol, the water being added at the double and not at the treble linking.
T. H. P.

Action of Potassium Hydroxide on a Mixture of Phenylacetylene and Methyl *iso*Propyl Ketone: Synthesis of Phenylacetylenylmethyl*iso*propylcarbinol. IWAN BORK (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 650—652. Compare preceding abstracts).—*Phenylacetylenylmethyl*iso*propylcarbinol*, $CHMe_2\cdot CMe(OH)\cdot C⋮CPh$, prepared by the interaction of phenylacetylene and methyl *iso*propyl ketone in presence of potassium hydroxide, melts at 41° and boils at 136—137° under 12 mm. pressure. On boiling with 10 per cent. potassium hydroxide solution, it is resolved into phenylacetylene and methyl *iso*propyl ketone. When boiled with 5 per cent. sulphuric acid solution, it yields a *hydrocarbon*, $CMe_2:CMe\cdot C⋮CPh$, which is a mobile liquid boiling at 120—122° under 12 mm. pressure, and having the sp. gr. 0·9409 at 0°/0° and 0·9254 at 20°/20°.
T. H. P.

Action of Potassium Hydroxide on a Mixture of Phenylacetylene and Pinacolin: Synthesis of Phenylacetylenylmethyl*tert.*-butylcarbinol. N. NEWEROWITSCH (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 652—654. Compare preceding abstracts).—*Phenylacetylenylmethyl*tert.*-butylcarbinol,* $CMe_3 \cdot CMe(OH) \cdot C⋮CPh$, obtained by the action of potassium hydroxide on a mixture of phenylacetylene and pinacolin, is an oily liquid boiling at 135—136° under 10 mm. pressure and having the sp. gr. 0·9855 at 0°/0° and 0·9694 at 20°/20°. When boiled with 10 per cent. potassium hydroxide solution, the alcohol is decomposed into phenylacetylene and pinacolin.

Dehydration of the alcohol by means of 5 per cent. sulphuric acid solution yields a *hydrocarbon*, $CH_2:C(CMe_3) \cdot C⋮CPh$, which is a mobile liquid boiling at 115—116° under 10 mm. pressure, and gradually changing into a solid polymeride when kept in a sealed tube.

T. H. P.

Action of Potassium Hydroxide on a Mixture of Phenylacetylene and Methyl*cyclo*hexanone. Ew. BERTROND (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 655—656).—The interaction of phenylacetylene and methyl*cyclo*hexanone in presence of potassium hydroxide yields an *alcohol*, $CH_2<\begin{matrix}CHMe \cdot CH_2\\CH_2—CH_2\end{matrix}>C(OH) \cdot C⋮CPh$, which crystallises from ether in thin, silky needles melting at 99° and dissolves slightly in alcohol. When heated with fused potassium hydrogen sulphate in a sealed tube, it yields resinous products and a *hydrocarbon*, $CH_2<\begin{matrix}CHMe \cdot CH\\CH_2—CH_2\end{matrix}>C \cdot C⋮CPh$ or $CH_2<\begin{matrix}CHMe \cdot CH_2\\CH_2—CH\end{matrix}>C \cdot C⋮CPh$, which boils at 167—168° under 10 mm. pressure.

T. H. P.

Action of Potassium Hydroxide on a Mixture of Phenylacetylene and Acetophenone. Ew. BERTROND (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 657).—The tertiary alcohol, $OH \cdot CMePh \cdot C⋮CPh$, obtained by the interaction of phenylacetylene and acetophenone in presence of potassium hydroxide, is identical with the compound obtained by Nef (Abstr., 1900, i, 20) as the result of the action of the sodium derivative of phenylacetylene on acetophenone.

T. H. P.

Action of Potassium Hydroxide on a Mixture of Phenylacetylene and Menthone. E. ROMANOFF (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 657—659).—The action of phenylacetylene on menthone in presence of potassium hydroxide yields an *alcohol*,

$$\begin{matrix}CH_2—CH_2—CH \cdot CHMe_2\\ | \qquad\qquad\quad | \qquad\quad\\ CHMe \cdot CH_2 \cdot C(OH) \cdot C⋮CPh\end{matrix},$$

which is a viscous, pale yellow liquid with a smell resembling that of menthone and a bitter taste; it boils at 196—198° under 14 mm. pressure, and has the sp. gr. 1·00449 at 0°/0° and 0·99056 at 20°/20°. On boiling with 10 per cent. potassium hydroxide solution, the alcohol is resolved into menthone and phenylacetylene, but it could not be dehydrated into the corresponding unsaturated hydrocarbon.

T. H. P.

Reversible Isomeric Process taking place between γ-Phenylpropylene and s-Phenylmethylethylene [α-Phenylpropylene] on heating with Anhydrous Alkali Hydroxide. M. Ageewa (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 662—668).—Treatment of γ-phenylpropyl alcohol with phosphorus and iodine yields the corresponding *iodide*, which is a viscous, pale rose-coloured liquid boiling at 127—129° under 9—10 mm. pressure, and having the sp. gr. 1·5781 at 0°/0° and 1·5613 at 20°/0°. When heated with anhydrous potassium hydroxide in a copper vessel, the iodide yields: (1) the *ether*, $(CH_2Ph\cdot CH_2\cdot CH_2)_2O$, which is a yellow liquid boiling at 220—222° under 19 mm. pressure, and having the sp. gr. 1·00797 at 0°/0° and 0·99488 at 17°/0°; the ether has the normal molecular weight in freezing benzene, and when heated with hydriodic acid gives the original iodide; (2) *γ-phenylpropylene*, $CH_2Ph\cdot CH{:}CH_2$, which boils at 157—160° and has the sp. gr. 0·90706 at 0°/0° and 0·8929 at 20·5°/0°; with bromine it gives *βγ-dibromo-α-phenylpropane*, $CH_2Ph\cdot CHBr\cdot CH_2Br$, which boils at 136—137° under 8 mm. pressure and has the sp. gr. 1·6902 at 0°/0° and 1·6613 at 23°/0°; (3) α-phenylpropylene, $CHPh{:}CHMe$, which boils at 172—175° and has the sp. gr. 0·93591 at 0°/0° and 0·90902 at 23°/0° (compare Wagner, *J. Russ. Phys. Chem. Soc.*, 1884, **16**, 324).

It is found that α-phenylpropylene is not a product of the original reaction, but is formed from γ-phenylpropylene by isomeric change effected by the agency of the alkali, a change which is shown to be reversible. T. H. P.

β-Amino-β-phenylpropionic Acid. Theodor Posner (*Ber.*, 1905, **38**, 2719).—An addendum to a paper recently published (this vol., i, 577).

Phenyldihydrothiouracil separates from alcohol in leaflets and melts at 240—242°. A. McK.

Condensation of Phenacylaniline with certain Chloro-ethers. Concetto Maselli (*Gazzetta*, 1905, **35**, ii, 86—94).—Considering the ease with which the hydrazones of γ-keto-acids give up a molecule of water yielding heterocyclic compounds (compare Ach, Abstr., 1890, 70), the author has attempted, but without success, to arrive at α-triazine derivatives by starting from phenylhydrazine and γ-keto-acids containing a nitrogen atom in their atomic chain.

Phenylphenacylurethane, $CH_2Bz\cdot NPh\cdot CO_2Et$, obtained by the interaction of molecular proportions of phenacylaniline and ethyl chlorocarbonate in an anhydrous solvent, crystallises from light petroleum in long, colourless prisms or tufts of small prisms melting at 66°. When heated at about 180° or boiled with an excess of alcoholic potassium hydroxide, phenylphenacylurethane yields: (1) an *iso*nitrile and (2) *diphenyloxazolone*, $CH{<}\begin{matrix}CPh\cdot O\\ NPh\cdot CO\end{matrix}$, which crystallises from benzene in white, shining needles melting at 171°.

Phenylphenacyloxamethane, $CH_2Bz\cdot NPh\cdot CO\cdot CO_2Et$, prepared from phenacylaniline and ethyl chloro-oxalate, crystallises from light petroleum in white, silky prisms melting at 90°. When heated at

about 200°, it yields a *lactone*, which crystallises from benzene in yellow prisms, melting and decomposing at 205°. T. H. P.

Claisen's Cinnamic Acid Synthesis. RICHARD STOERMER and OTTO KIPPE (*Ber.*, 1905, 38, 3032—3036. Compare this vol., i, 526; Michael, *ibid.*, i, 646).—Claisen's synthesis of cinnamic acid (Abstr., 1890, 891) has been repeated, using ten times the theoretical amount of ethyl acetate. The brown salt formed was removed and washed with dry ether, care being taken to exclude moisture. The filtrate contains ethyl cinnamate in quantity equal to that obtained by Claisen when dilute acid was employed. The solid salt consists of 80 per cent. of sodium acetate together with sodium cinnamate and resinous substances. These facts cannot be reconciled with Michael's view that a salt $ONa\cdot CHPh\cdot CH_2\cdot CO_2Et$ is formed, which is decomposed subsequently by water into sodium hydroxide and ethyl cinnamate. The elimination of sodium hydroxide must occur during the condensation and before water is added.

Similar results have been obtained in the synthesis of ethyl phenoxycinnamate. Similarly, when sodium reacts with a dry ethereal solution of ethyl β-hydroxy-α-phenoxycinnamate, a white salt is formed, and the ethereal solution contains pure ethyl phenoxycinnamate. When only the theoretical amount of ethyl acetate is used in the ethyl cinnamate synthesis, considerable amounts of sodium cinnamate are formed due to the hydrolysing action of the sodium hydroxide liberated. J. J. S.

Formation of Isomeric Hydrocinnamylideneacetic Acids. C. N. RIIBER (*Ber.*, 1905, 38, 2742—2748. Compare Abstr., 1904, i, 894).—Cinnamylideneacetic acid is obtained in good yield when cinnamylidenemalonic acid is sublimed under 0·3 mm. pressure.

$\alpha\delta$-Dihydrocinnamylideneacetic acid is readily obtained by distilling $\alpha\delta$-dihydrocinnamylidenemalonic acid at 0·15 mm. pressure, when it boils at 127—128°; it melts at 31°. When its methyl ester is oxidised, a mixture of phenylacetic, benzoic, and malonic acids is formed.

$\gamma\delta$-Dihydrocinnamylideneacetic acid forms oxalic and hydrocinnamic acids when oxidised by alkaline permanganate.

When $\gamma\delta$-dihydrocinnamylidenemalonic acid is heated under diminished pressure, $\alpha\delta$-dihydrocinnamylideneacetic acid is formed, and not the $\gamma\delta$-acid.

When $\alpha\delta$-dihydrocinnamylidenemalonic acid is boiled with water or benzene, the double linking is shifted towards the carboxyl group, so that the $\gamma\delta$-dihydromalonic acid is formed, and when this is heated the double linking is again shifted to its original position, thus:

(1) $CH_2Ph\cdot CH\!:\!CH\cdot CH(CO_2H)_2 \longrightarrow CH_2Ph\cdot CH_2\cdot CH\!:\!C(CO_2H)_2$.
(2) $CH_2Ph\cdot CH_2\cdot CH\!:\!C(CO_2H)_2 \longrightarrow CH_2Ph\cdot CH\!:\!CH\cdot CH_2\cdot CO_2H$.

As products of the action of sodium hydroxide on $\alpha\delta$-dihydrocinnamylideneacetic acid, the author has isolated $\gamma\delta$-dihydrocinnamylideneacetic acid, β-hydroxyphenylvaleric acid, $\alpha\beta$-dihydrocinnamylideneacetic acid, and an unsaturated acid, $C_{11}H_{12}O_2$, which is possibly an isomeric

$\alpha\delta$-dihydro-acid. When $\alpha\beta$-dihydrocinnamylideneacetic acid is oxidised by alkaline permanganate, benzoic and succinic acids are formed.

A. McK.

Benzoylation of Salicylamide. Alfred Einhorn and Gustav Schupp (*Ber.*, 1905, **38**, 2792—2798. Compare Limpricht, *Annalen*, 1856, **99**, 249).—Gerhardt and Chiozza's (*Jahresber.*, 1856, 502) benzoylsalicylamide is shown to be the *N*-benzoyl derivative,

$OH{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}COPh.$

The same benzoyl derivative is obtained by the action of methyl salicylate on the sodium derivative of benzamide (Titherley, Trans., 1902, **81**, 1520, gives the melting point 122°; this should be 200—202°) or by benzoylating salicylamide in pyridine solution.

When further benzoylated, it yields a *dibenzoyl* derivative,

$COPh{\cdot}O{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}COPh,$

which dissolves in most organic solvents with the exception of ether, crystallises from alcohol in small needles melting at 126—128°, gives no coloration with ferric chloride, is insoluble in dilute hydrochloric acid, and is decomposed by potassium hydroxide, both benzoyl groups being eliminated. A *tribenzoyl* derivative,

$COPh{\cdot}O{\cdot}C_6H_4{\cdot}CO{\cdot}N(COPh)_2,$

is obtained when the dibenzoyl compound is carefully benzoylated by the Schotten-Baumann method. It crystallises from hot alcohol or xylene in prismatic needles, melts at 182—184°, gives no colour reaction with ferric chloride, and is insoluble in dilute acids or alkalis. When heated with pyridine, it yields *N*-benzoylsalicylamide, or with potassium hydroxide, salicylamide and benzoic acid.

N-Benzoylsalicylamide forms an *additive compound* with its sodio-derivative (Limpricht), namely, $C_{28}H_{21}O_6N_2Na$, which crystallises from alcohol in golden-yellow needles. The same compound is formed when carbon dioxide is passed into a solution of benzoylsalicylamide in sodium hydroxide. A *piperidine* salt,

$OH{\cdot}C_6H_4{\cdot}CO{\cdot}NH(COPh),C_5NH_{11},$

is obtained by the addition of piperidine to an alcoholic solution of the benzoyl derivative. It crystallises in yellow needles and melts at 145—147°. It forms a colourless additive product with *N*-benzoyl-salicylamide, probably

$OH{\cdot}C_5NH_{11}{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}COPh,OH{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}COPh,$

which melts at 153—155°.

J. J. S.

By-products from the Preparation of Piperonalindigo and its Oxidation. Paul Herz (*Ber.*, 1905, **38**, 2853—2860. Compare Book, Abstr., 1902, i, 464; 1903, i, 653).—The following four substances are obtained as by-products from the preparation of bis-methylenedioxyindigo (piperonalindigo) (Liebermann and Haber, Abstr., 1890, 1140):

(1) o-*Nitropiperonylhydracryl methyl ketone*,

$CH_2{:}O_2{:}C_6H_2(NO_2){\cdot}CH(OH){\cdot}CH_2{\cdot}COMe,$

which represents the first stage in the formation of piperonalindigo from nitropiperonal and acetone, crystallises in long, yellow plates,

melts at 145°, forms piperonalindigo when treated with sodium hydroxide, and when boiled with acetic anhydride yields *o*-nitropiperonylacryl methyl ketone. The *phenylhydrazone*, $C_{17}H_{17}O_5N_3$, crystallises in yellow leaflets and melts and decomposes at 134—139°. The *oxime*, $C_{11}H_{12}O_6N_2,H_2O$, crystallises in yellow needles, melts at 78—83°, loses H_2O in the desiccator or at 100°, and when anhydrous melts at 130°. 4-*Hydroxy*-6 : 7-*methylenedioxy*-2-*methylquinoline*,

$$CH_2{:}O_2{:}C_6H_2{<}\begin{matrix}C(OH){\cdot}CH \\ | \\ N{=\!=}CMe\end{matrix},$$

formed by reduction of *o*-nitropiperonylhydracryl methyl ketone with zinc dust in boiling aqueous solution, crystallises in white needles and melts at 185°. The *hydrochloride*, $C_{11}H_9O_3N,HCl$, crystallises in silky needles and melts at 230—235° with decomposition; the *platinichloride*, $(C_{11}H_9O_3N)_2,H_2PtCl_6$, forms orange needles and melts at 234°; the *acetyl* derivative, $C_{13}H_{11}O_4N$, crystallises in colourless needles and melts at 110°.

(2) *o*-Nitropiperonylacryl methyl ketone (Haber, Abstr., 1891, 705) forms an *oxime*, $C_{11}H_{10}O_5N_2$, which crystallises in yellow leaflets and melts and decomposes at 220°.

(3) *Di*-o-*nitrodipiperonylhydracryl ketone*,

$$[CH_2{:}O_2{:}C_6H_2(NO_2){\cdot}CH(OH){\cdot}CH_2]_2CO,$$

crystallises in colourless needles, melts at 195°, is insoluble in boiling water, but moderately soluble in alcohol or acetone, and when boiled with acetic anhydride yields di-*o*-nitrodipiperonylacryl ketone (Haber, *loc. cit.*).

(4) Nitromethylenecatechol (Jobst and Hesse, Abstr., 1878, 1733) is obtained from the crude product from the interaction of nitropiperonal and acetone by sublimation.

5 : 6-*Methylenedioxyisatin*, $CH_2{:}O_2{:}C_6H_2{<}\begin{matrix}CO \\ -N\end{matrix}{>}C{\cdot}OH$, formed by warming piperonalindigo with dilute nitric acid, crystallises in dark red needles, melts and decomposes at 280°, dissolves in concentrated sulphuric acid to form a blue solution, from which it is precipitated in needles on adding water, and with thiophen and sulphuric acid forms *dioxymethyleneindophenin*, $C_{13}H_7O_3NS$, as a blue precipitate.

3-*Nitro*-4 : 5-*methylenedioxyanthranilic acid*,

$$CH_2{:}O_2{<}\begin{matrix}C{\cdot}CH{=\!=}C{\cdot}CO_2H \\ \| \qquad\quad | \\ C{\cdot}C(NO_2){:}C{\cdot}NH_2\end{matrix},$$

formed by the action of nitric acid on piperonalindigo, crystallises in yellow needles, forms aqueous and alcoholic solutions with green fluorescence, and when warmed in alkaline solution loses carbon dioxide and yields *nitroaminomethylenecatechol*, $CH_2{:}O_2{<}\begin{matrix}C{\cdot}CH{=\!=}CH \\ \| \qquad | \\ C{\cdot}C(NO_2){:}C{\cdot}NH_2\end{matrix}$. This crystallises in orange leaflets, melts at 195°, is soluble in hot water or hydrochloric acid, and is precipitated from its concentrated solution in concentrated hydrochloric acid on addition of water. When reduced with zinc dust in boiling aqueous solution, this forms *diaminomethylenecatechol*, which in solution gives the reactions for ortho-diamines and on oxidation yields a yellow, sparingly soluble *base*, which behaves as a diaminophenazine.

Methylenedioxyphenophenanthrazine,

$$CH_2{:}O_2{<}\begin{matrix}C{\cdot}CH{:}CH{\cdot}C{\cdot}N{:}C{\cdot}C_6H_4 \\ \| \qquad\qquad \| \quad\; | \quad | \\ C{-\!-\!-\!-\!-\!-}C{\cdot}N{:}C{\cdot}C_6H_4\end{matrix},$$

is formed by reduction of nitroaminomethylenecatechol with zinc dust in alcoholic glacial acetic acid solution, and addition of phenanthraquinone to the diamine solution so formed. It crystallises in yellow needles, melts at 309°, dissolves easily in glacial acetic acid, but only sparingly in alcohol, to form violet, fluorescent solutions, and forms a reddish-violet solution in concentrated sulphuric acid. G. Y.

Phenyl Ether-*o*-carboxylic [Aryloxybenzoic] Acids. Aktien-Gesellschaft für Anilin-Fabrikation (D.R.-P. 158998. Compare Abstr., 1904, i, 499).—Sodium phenoxide, or the alkali derivatives of other phenols, reacts readily with *o*-chlorobenzoic acid in presence of copper or copper salts to form *o*-carboxylic acids of the corresponding phenyl ether.

o-*Tolyloxybenzoic acid* separates from a mixture of benzene and light petroleum in coarse crystals and melts at 130°; p-*tolyloxybenzoic acid* forms large crystals and melts at 117°; *β-naphthyloxybenzoic acid* forms colourless crystals and melts at 121°. The acids are insoluble in water, and dissolve readily in alcohol or benzene. C. H. D.

Enantiomorphism of the *cyclo*Propanecarboxylic Acids. Eduard Buchner and Richard von der Heide (*Ber.*, 1905, **38**, 3112—3119).—*r-trans-cyclo*Propane-1 : 2-dicarboxylic acid can be resolved into its optically active components by means of brucine, quinine, or cinchonidine in aqueous solution.

The d-*acid*, $C_5H_6O_4$, melts at 175°, and has $[\alpha]_D$ +84·42—84·87° at 26°. Its *brucine* salt, $2C_{23}H_{26}O_4N_2,C_5H_6O_4,6H_2O$, crystallises slowly from the cold aqueous solution and loses $6H_2O$ at 120°; the *acid-quinine* salt, $C_{20}H_{24}O_2N_2,C_5H_6O_4,2H_2O$, crystallises from the cold aqueous solution in stellate aggregates of hexagonal crystals and loses $2H_2O$ at 125°; the *cinchonidine* salt is soluble in cold water.

The l-*acid* melts at 175° and has $[\alpha]_D$ −84·40—84·53° at 27°. Its *cinchonidine* salt, $C_{19}H_{22}ON_2,C_5H_6O_4,2H_2O$, crystallises from the aqueous solution on cooling and loses $2H_2O$ at 125°; the *brucine* and *quinine* salts are soluble in cold water.

*r-cyclo*Propane-1 : 1 : 2-tricarboxylic acid can be resolved into its active components in the same manner as *r-trans-cyclo*propane-1 : 2-dicarboxylic acid. The d-*acid* decomposes at 187° and has $[\alpha]_D$ +84·57° at 26°. The *brucine* salt, $C_{52}H_{58}O_{14}N_4,4H_2O$, loses $4H_2O$ at 130°; the *quinine* salt, $C_{46}H_{54}O_{10}N_4,2H_2O$, loses $2H_2O$ at 130°. The l-*acid* has $[\alpha]_D$ −84·65° at 26°; the *cinchonidine* salt, $C_{25}H_{28}O_7N_2$, is anhydrous at 130°.

*cis-cyclo*Propane-1 : 2- and *cyclo*propane-1 : 1-dicarboxylic and *cis-trans-cyclo*propane-1 : 2 : 3-tricarboxylic acids cannot be resolved into optically active components.

*cis-cyclo*Propane-1 : 2 : 3-tricarboxylic acid was not investigated.

G. Y.

Condensation of Benzil with Resorcinol. I. Non-fluorescent Substances. HANS VON LIEBIG (*J. pr. Chem.*, 1905, [ii], 72, 105—172. Compare Abstr., 1899, i, 915; 1903, i, 828, 829).—Benzil, resorcinol, and sodium sulphate are heated together at 180—200° for 7—8 hours, and the cooled product washed and treated with aqueous potassium hydroxide. After being washed with hydrochloric acid and water, the undissolved portion of the product, on treatment with alcohol, yields 4-hydroxy-2-ethoxytritanic anhydride, 2 : 4-dihydroxytritanolactone, 3 : 5-dihydroxytritanolactone, a compound, $C_{40}H_{28}O_5$, which is obtained as a sandy-red powder, and the anhydride of this, $C_{40}H_{26}O_4$, which forms a yellowish-brown or red powder. On extraction with ether, the aqueous alkaline solution yields resorcinolbenzein, 3 : 5-dihydroxytritanic acid and its lactone, 3 : 5-dihydroxytritanic lactone ether, 4-hydroxy-2-ethoxyltritanic anhydride, and two substances which are probably identical with Barth and Weidel's resorcinyl ethers, $C_{12}H_{10}O_3$ and $C_{24}H_{18}O_8$ (Abstr., 1878, 61).

The name tritanic acid is used in place of triphenylmethanecarboxylic (triphenylacetic) acid.

2 : 4-*Dihydroxytritanolactone*, $\begin{array}{l} CPh_2\text{—}C\cdot C(OH)\text{:}C \\ CO\cdot O\cdot C\text{—}CH\text{—}C\cdot OH \end{array}$, crystallises from benzene in small, rhombic leaflets containing benzene of crystallisation, melts at 264°, is slightly less soluble than 3 : 5-dihydroxytritanolactone, and dissolves in alcohol to form a solution which on exposure to air becomes green and finally a dirty brown.

3 : 5-*Dihydroxytritanic acid*, $C_6H_3(OH)_2\cdot CPh_2\cdot CO_2H,H_2O$, crystallises in flocculent aggregates of needles on addition of acetic acid to the aqueous solution of its tripotassium salt; it melts with effervescence in a capillary tube at 120—130°, and changes into the lactone slowly at the ordinary temperature, more quickly on the water-bath, or immediately at 120°. The acid crystallises from its ethereal and alcoholic solutions in rhombohedra containing ether and alcohol respectively of crystallisation. The stability of this acid is in agreement with the positions 3 and 5 assigned to the hydroxyl groups. The *sodium* salt, $C_{20}H_{15}O_4Na,2H_2O$, crystallises in small clusters of needles or hexagonal prisms; the *potassium* salt, $C_{20}H_{15}O_4K,2H_2O$, crystallises in long, slender needles; $C_{20}H_{15}O_4K,C_2H_6O$ crystallises in rectangular plates; the *ammonium*, $C_{20}H_{15}O_4NH_4,H_2O$, the *trisodium*,

$$C_{20}H_{13}O_4Na_3,C_2H_6O,4H_2O$$

or $C_{20}H_{13}O_4Na_3,4\frac{1}{2}H_2O$, and *tripotassium*, $C_{20}H_{13}O_4K_3,CH_4O,4H_2O$, salts are described. The lactone crystallises from benzene in colourless leaflets, or from alcohol in large, monoclinic rhombohedra, and decomposes with formation of diphenylmethane when heated under the atmospheric pressure, but distils partly unchanged in a vacuum. It is precipitated from its boiling alcoholic solution by a current of hydrogen chloride, gives with concentrated sulphuric acid a yellow coloration which gradually becomes red, and dissolves in aqueous alkali hydroxides to form solutions which become brown on exposure to air. The substance melting at 120°, and previously supposed to be the monoacetyl derivative (Abstr., 1903, i, 828), is now found to be a mixture of the lactone and its acetyl derivative, $C_{20}H_{14}O_2Ac$, which

melts at 161° and was termed previously the diacetyl derivative. The supposed dibenzoyl derivative has the formula $C_{20}H_{14}O_2Bz$.

Methyl 3 : 5-*dimethoxytritanate*, $C_6H_3(OMe)_2\cdot CPh_2\cdot CO_2Me$, formed by the action of warm methyl sulphate on 3 : 5-dihydroxytritanic lactone in warm aqueous potassium hydroxide solution, crystallises in glistening, rhombic leaflets, melts at 168°, gives a blood-red coloration with sulphuric acid, and is only partly hydrolysed by prolonged boiling with alcoholic potassium hydroxide or by treatment with fused potassium hydroxide at 150°, with formation of the corresponding dimethoxy-acid.

The action of methyl sulphate on 3 : 5-dihydroxytritanolactone in aqueous alkali hydroxide solution at the ordinary temperature leads to the formation of 3 : 5-dimethoxytritanic acid and of 5-methoxy-3-hydroxytritanolactone.

3 : 5-*Dimethoxytritanic acid*, $C_{22}H_{20}O_4$, crystallises in four-sided prisms, melts at 246°, decomposes and evolves gas at 300°, gives a blood-red coloration with sulphuric acid, and forms its methyl ester when shaken with methyl sulphate and aqueous potassium hydroxide. The *sodium* salt (with $2H_2O$) crystallises in long, slender needles; the *potassium* salt, $C_{22}H_{19}O_4K,2H_2O$, forms long, spicular needles; the *ammonium* salt (with $2H_2O$) crystallises in clusters of short, slender needles. The *barium*, *copper*, and *silver* salts are described.

The action of boiling acetyl chloride on the dimethoxy-acid leads to the formation of 3-*hydroxy*-5-*methoxytritanolactone*, $C_{21}H_{16}O_3$, which crystallises in long rhombohedra, melts at 180—181°, is almost insoluble in aqueous potassium hydroxide on the water-bath, but dissolves on boiling to form a solution from which, on acidification, 3-*hydroxy*-5-*methoxytritanic acid* is precipitated; this, when heated on the water-bath, is reconverted into the lactone.

The action of ethyl sulphate on 3 : 5-dihydroxytritanolactone in aqueous alkali hydroxide solution leads to the formation of 3 : 5-diethoxytritanic acid and its ethyl ester and hydroxyethoxytritanolactone.

3 : 5-*Diethoxytritanic acid*, $C_6H_3(OEt)_2\cdot CPh_2\cdot CO_2H$, crystallises in small, rectangular leaflets and melts at 181—182°. The *ethyl* ester, $C_{36}H_{28}O_4$, crystallises in slender, white needles, melts at 122°, and gives a red coloration with sulphuric acid, but more slowly than the corresponding methyl derivative. 3-*Hydroxy*-5-*ethoxytritanolactone*, $C_{22}H_{18}O_3$, crystallises in rhombic leaflets and melts at 151—152°.

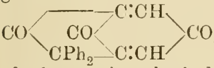
When tripotassium 3 : 5-dihydroxytritanate is heated for eight hours on the water-bath and the product treated with water and hydrochloric acid, there is obtained a *substance*, $C_{40}H_{30}O_7$, as a yellowish-brown powder, which is formed also by the action of a current of air on the alkaline solution of the acid. The action of fused potassium hydroxide on 3 : 5-dihydroxytritanolactone leads to the formation of diphenylmethane, resorcinol, resorcylic and benzoic acids, and a *substance*, $C_{28}H_{30}O_4$, which is formed also when the tripotassium salt is heated at 240°. This sinters and decomposes at about 160°, and dissolves in alcoholic potassium hydroxide, forming a brownish-red solution with intense green fluorescence.

When heated at 300°, potassium 3 : 5-dihydroxytritanate yields (1)

a small amount of diphenylmethane, (2) the phenol *ether* of 3 : 5-dihydroxytritanol, $O\left[\begin{array}{l}CH\cdot C(OH){:}CH \\ C\cdot CH{=\!=}C\cdot CPh_2\cdot OH\end{array}\right]_2$, which dissolves in water to form a blue fluorescent liquid, in aqueous ammonia or alkali hydroxides or carbonates to form brownish-red solutions with slight blue fluorescence, which becomes green on addition of alcohol, and (3) 3 : 5-*dihydroxytritane ether*, $O[C_6H_3(OH)\cdot CHPh_2]_2$, which is insoluble in water but dissolves in alcohol or aqueous alkali hydroxides to form solutions with green fluorescence, which becomes blue on dilution with water.

If 3 : 5-dihydroxytritanolactone is warmed with concentrated sulphuric acid and the product treated with ammonium sulphate, there is formed the *ammonium sulphonate*, $C_{20}H_{13}O_3\cdot SO_3NH_4,1\frac{1}{2}H_2O$, which crystallises from water in spicular needles, or from alcohol with alcohol of crystallisation, melts when anhydrous at 224—225°, and gives a reddish-violet coloration with aqueous ferric chloride.

Oxidation of 3 : 5-dihydroxytritanolactone with lead peroxide in glacial acetic acid solution leads to the formation of a *substance*,



which forms a red, sandy powder, consisting of microscopic, spherical crystals, which melts above 290°. Oxidation of the lactone with chromic acid in glacial acetic acid solution leads to the formation of benzophenone, or with alkaline permanganate to the formation of benzophenone and a number of intermediate products.

Diphenylmethane was obtained by the distillation of 3 : 5-dihydroxytritanolactone.

3 : 5-*Dihydroxytritanolactone ether*, $O(C_{20}H_{13}O_2)_2$, crystallises in rhombic or hexagonal leaflets, melts at 224°, gives a blood-red coloration with concentrated sulphuric acid, and when distilled is decomposed with formation of diphenylmethane and a *substance* which dissolves in benzene to form a reddish-brown solution with green fluorescence. The *sodium* salt, $O(C_{20}H_{13}O_3Na_2)_2$, which forms glistening needles, and the *potassium* salt, $O(C_{20}H_{13}O_3K_2)_2$, were analysed. The *ether* of methyl 3 : 5-dimethoxytritanate, $O[C_6H_3(OMe)\cdot CPh_2\cdot CO_2Me]_2$, formed by the action of methyl sulphate and aqueous potassium hydroxide on the potassium salt, crystallises in spicular needles, melts at 176°, and gives a blood-red coloration with concentrated sulphuric acid. Together with the ester there is formed a *substance* which melts at 91°, decomposes and evolves gas at 150°, and is more soluble in alcohol.

The *ether* of 3 : 5-dimethoxytritanic acid, $O[C_6H_3(OMe)\cdot CPh_2\cdot CO_2H]_2$, is formed by the hydrolysis of its ester by means of potassium hydroxide or by the action of methyl sulphate on potassium dihydroxytritanate ether in presence of an excess of potassium hydroxide. It crystallises in small, spicular needles and melts and decomposes at 274°, or sometimes at 304°. G. Y.

Condensation of α-Keto-acids with Aldehydes by means of Hydrochloric Acid or Sodium Hydroxide. EMIL ERLENMEYER, jun. (*Ber.*, 1905, **38**, 3119—3125. Compare Abstr., 1903, i,

698).—Phenylpyruvic acid and benzaldehyde condense with sodium hydroxide in aqueous solution to form *sodium γ-hydroxy-α-keto-βγ-diphenylbutyrate*, which separates slowly in colourless crystals, and on addition of hydrochloric acid yields the free *acid*,

$$OH\cdot CHPh\cdot CHPh\cdot CO\cdot CO_2H.$$

This separates from alcohol in glistening crystals, melts at 175°, is soluble in ether, and has a strong acid reaction. When warmed with an excess of aqueous sodium hydroxide, it decomposes with formation of benzaldehyde, and when warmed with hydrochloric acid is converted into α-keto-βγ-diphenylbutyrolactone, melting at 206°. The α-keto-acid forms with hydroxylamine an amorphous *oxime* melting at 96°, and with phenylhydrazine the *phenylhydrazone*, $NHPh\cdot N:C<\begin{matrix}CHPh\cdot CHPh\\ CO\text{---}O\end{matrix}$, melting at 188°. With phenylhydrazine, α-keto-βγ-diphenylbutyrolactone forms a *phenylhydrazine* salt, $C_{22}H_{20}O_3N_2$, melting at 136°.

Reduction of γ-hydroxy-α-keto-βγ-diphenylbutyric acid with sodium amalgam leads to the formation of an *α-hydroxy-βγ-diphenylbutyrolactone*, which separates from chloroform on addition of light petroleum as a microcrystalline powder and melts at 127°, and of an *isomeride* which crystallises from alcohol in small needles, melts at 171°, and is insoluble in chloroform. Both these products yield desylacetic acid when boiled with dilute hydrochloric acid; together with the two products melting at 127° and 170° obtained by Erlenmeyer and Lux (Abstr., 1898, i, 668) by reduction of α-keto-βγ-diphenylbutyrolactone, with which they are not identical; they form two pairs of stereoisomerides and all the four possible racemic modifications of α-hydroxy-βγ-diphenylbutyrolactone are now known. The melting points of a number of stereoisomeric racemic α-hydroxybutyrolactones are given to show that close agreement of the melting points of the pairs of stereoisomerides is not uncommon.

When treated with concentrated sodium hydroxide, α-keto-βγ-diphenylbutyrolactone is hydrolysed to the γ-hydroxy-acid melting at 175°; this, on reduction with sodium amalgam in concentrated solution, yields phenyl-α-lactic acid and two products which are not obtained by reduction of the lactone. (1) The *dilactone*,

$$CHPh<\begin{matrix}CHPh\\ O\text{--}CO\end{matrix}>C(OH)\cdot C(OH)<\begin{matrix}CHPh\\ CO\text{--}O\end{matrix}>CHPh,$$

crystallises in transparent prisms, melts at 236°, has a neutral reaction, and forms a sparingly soluble *barium* salt. (2) s-*Dibenzyltartaric acid*, $CO_2H\cdot C(OH)(CH_2Ph)\cdot C(OH)(CH_2Ph)\cdot CO_2H$, crystallises from chloroform, melts at 212°, is soluble in sodium hydrogen carbonate solution, and forms a sparingly soluble *barium* salt; the *potassium* and *silver* salts were analysed. As this acid is formed only in small quantity by reduction of phenylpyruvic acid by means of sodium amalgam in concentrated solution, but in large quantity by reduction with zinc and hydrochloric acid, it is formed probably by decomposition of a reduction product of γ-hydroxy-α-keto-βγ-diphenylbutyric acid. The condensation of benzaldehyde and pyruvic acid in presence of sodium hydroxide or hydrochloric acid leads to the formation of two stereoisomeric cinnamylformic acids. Erlenmeyer and Stirm's solid acid forms a crystalline *phenylhydrazone* melting at

162°, and is converted by concentrated hydrochloric acid into Claisen and Claparède's oily acid (Abstr., 1882, 520). This forms an amorphous *phenylhydrazone*, $C_{16}H_{14}O_2N_2$, melting at 94°, and on reduction yields an amorphous *a-hydroxyphenyl*iso*crotonic acid*, $C_{16}H_{10}O_3$?, which is converted by boiling hydrochloric acid into benzoylpropionic acid. When dissolved in aqueous sodium hydroxide, Claisen and Claparède's oily acid is slowly converted into the sodium salt of Erlenmeyer and Stirm's solid acid. G. Y.

Preparation of $\alpha\beta$- and $\beta\gamma$-Unsaturated Lactones. EMIL ERLENMEYER, jun. (*Ber.*, 1905, **38**, 3125—3129. Compare Abstr., 1904, i, 892; Thiele, Abstr., 1899, i, 216).—The unsaturated *acid*, $OMe\cdot C_6H_4\cdot CH:CPh\cdot CH(OH)\cdot CO_2H$, is formed by boiling α-oxy-β-phenyl-γ-methoxyphenylbutyrolactone with zinc dust in glacial acetic acid solution for three hours; it crystallises from chloroform and light petroleum in slender needles, melts at 126°, and when dissolved in acetic anhydride containing a small quantity of sulphuric acid and the mixture poured into water yields the labile, unsaturated lactone melting at 105°. The substance obtained previously (Erlenmeyer and Lattermann, Abstr., 1904, i, 1017), which melted at 145° and was supposed to be the $\beta\gamma$-unsaturated α-hydroxy-acid, was impure γ-keto-acid. When similarly reduced, the γ-keto-acid yields the stable, unsaturated lactone melting at 122°.

When treated with sulphuric acid and acetic anhydride, γ-oxy-β-phenyl-γ-*iso*propylphenylbutyric acid, melting at 111° (Erlenmeyer and Kehren, Abstr., 1904, i, 1015), yields a labile, unsaturated Δ^2-*lactone*, $C_{19}H_{18}O_2$, which separates from alcohol in stout crystals, melts at 122°, and easily changes into the stable, unsaturated Δ^1-lactone melting at 124°. Both lactones yield the same condensation product with benzaldehyde in presence of piperidine.

When treated with acetic anhydride and sulphuric acid, Erlenmeyer and Braun's $\beta\gamma$-unsaturated α-hydroxy-acid (Abstr., 1904, i, 1016) yields the stable lactone melting at 183°, which has, therefore, the ethylene linking in the $\alpha\beta$-position. The γ-keto-acid obtained on hydrolysis of the stable lactone on treatment with acetic anhydride and sulphuric acid yields a labile, unsaturated *lactone*,

$$CH_2:O_2:C_6H_3\cdot C\begin{cases} CPh\cdot CH_2 \\ O\text{——}CO \end{cases},$$

which by piperidine in alcoholic solution is converted into the stable lactone (m. p. 183°). Both lactones yield a condensation *product* with benzaldehyde, melting at 196°.

These facts support the author's view that an $\alpha\beta$-unsaturated lactone forms the intermediate product in the formation of γ-keto-acids from $\beta\gamma$-unsaturated α-hydroxy-acids. G. Y.

Acetylhydrocotarnineacetic Acid. WILHELM AHLERS (*Ber.*, 1905, **38**, 2873—2877. Compare Bowman, Abstr., 1887, 1056. Liebermann and Kropf, Abstr., 1904, i, 263).—*Hydrocotarnineacetic acid*, $CH_2:O_2:C_6H(OMe)(CH:CH\cdot CO_2H)\cdot CH_2\cdot CH_2\cdot NHMe$, prepared by the action of silver oxide on the hydrochloride (Bowman), is obtained in the crystalline state on evaporating the aqueous solution;

it melts at 116°, and when treated with hydrogen chloride in methyl alcoholic solution yields the *methyl* ester,

$CH_2{:}O_2{:}C_6H(OMe)(CH{:}CH{\cdot}CO_2Me){\cdot}CH_2{\cdot}CH_2{\cdot}NHMe$.

This crystallises from methyl alcohol and melts at 63°; the *platinichloride*, $(C_{15}H_{19}O_5N)_2,H_2PtCl_6$, forms a yellow, flocculent precipitate and decomposes, without melting, at 90°. The action of methyl iodide on the methyl ester leads to the formation of the *methiodide* of methyl methylhydrocotarnineacetate,

$CH_2{:}O_2{:}C_6H(OMe)(CH{:}CH{\cdot}CO_2Me){\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3I$,

which forms yellow crystals and melts at 119°.

Acetylhydrocotarnineacetic acid dibromide,

$CH_2{:}O_2{:}C_6H(OMe)(CHBr{\cdot}CHBr{\cdot}CO_2H){\cdot}CH_2{\cdot}CH_2{\cdot}NMeAc$,

formed by the action of bromine on the acid in glacial acetic acid solution, separates from alcohol in glistening, white crystals, melts at 188°, and is soluble in aqueous sodium carbonate. The *methyl* ester, $C_{17}H_{21}O_6NBr_2$, crystallises from aqueous methyl alcohol and melts at 121°.

Dihydroacetylhydrocotarnineacetic acid,

$CH_2{:}O_2{:}C_6H(OMe)(CH_2{\cdot}CH_2{\cdot}CO_2H){\cdot}CH_2{\cdot}CH_2{\cdot}NMeAc$,

formed by reduction of acetylhydrocotarnineacetic acid with sodium amalgam, melts at 176° and decolorises potassium permanganate only slowly.

Acetylcotarnine, $CH_2{:}O_2{:}C_6H(OMe)(CHO){\cdot}CH_2{\cdot}CH_2{\cdot}NMeAc$, is formed by the action of potassium permanganate on acetylhydrocotarnineacetic acid dissolved in aqueous sodium carbonate or by the action of a small quantity of acetic anhydride on cotarnine. It crystallises from alcohol and melts at 146°, and yields acetylcotarnineacetic acid when heated with sodium acetate and acetic anhydride at 100—120° in a sealed tube. The *oxime*, $C_{14}H_{18}O_5N_2$, melts at 156°.

Benzoylhydrocotarnineacetic acid,

$CH_2{:}O_2{:}C_6H(OMe)(CH{:}CH{\cdot}CO_2H){\cdot}CH_2{\cdot}CH_2{\cdot}NMeBz$,

formed by heating benzoylcotarnine with acetic anhydride and sodium acetate, crystallises in needles. The *ethyl* ester melts at 81°; the *silver* salt, $C_{21}H_{20}O_6NAg$, is obtained as a white precipitate. G. Y.

Preparation of Ethyl Tetramethylene-1 : 1-dicarboxylate. Nic. M. Kijner (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 507—509).—When Perkin's method is applied to the preparation of ethyl *cyclo*butane-1 : 1-dicarboxylate, from ethyl sodiomalonate (2 mols.) and $\alpha\gamma$-dibromopropane (1 mol.), poor yields are obtained and the ester is difficult to separate. Much better results are obtained by the interaction of ethyl sodiomalonate and α-chloro-γ-bromopropane, the reactions being represented by (1) $CHNa(CO_2Et)_2 + CH_2Br{\cdot}CH_2{\cdot}CH_2Cl = CH_2Cl{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CO_2Et)_2 + NaBr$ and

(2) $CH_2Cl{\cdot}CH_2{\cdot}CH_2{\cdot}CNa(CO_2Et) = CH_2{<}{}^{CH_2}_{CH_2}{>}C(CO_2Et)_2 + NaCl$.

Prepared in this way, the ester is easily separated and boils at 222—226°. T. H. P.

β-Benzylmalic Acid. Oscar Doebner and M. Kersten (*Ber.*, 1905, **38**, 2737—2742).—The method of preparation of β-benzylmalic

acid is analogous to that of ethylmalic acid (this vol., i, 737). Ethyl benzylmalonate was prepared according to Fittig and Röder's method by boiling together ethyl malonate, sodium ethoxide, and benzyl chloride in ethyl-alcoholic solution. Benzylmalonic acid, prepared by hydrolysing it, melts at 117°.

γ-Trichloro-β-hydroxy-α-benzylbutyric acid, prepared by heating benzylmalonic acid with chloral and pyridine for six hours at 60—70°, separates from a mixture of ethyl alcohol and water in glistening leaflets and melts at 182°. Its *silver*, *lead*, and *copper* salts were examined.

When heated with a 10 per cent. aqueous solution of potassium hydroxide, γ-trichloro-β-hydroxy-α-benzylbutyric acid is converted into potassium β-benzylmalate. *β-Benzylmalic acid*,

$$CO_2H\cdot CH(OH)\cdot CH(CH_2Ph)\cdot CO_2H,$$

separates from a mixture of ether and light petroleum in tiny crystals and melts at 155°. Its *silver*, *lead*, *copper*, *barium*, and *strontium* salts are described.

Phenylitaconic acid is produced when β-benzylmalic acid is heated at 200°, whilst phenylcitraconic acid is formed probably as an intermediate product. A. McK.

Action of Ethyl Sodiomalonate on Sodium Salts of Unsaturated Acids. GUSTAV REINICKE (*Annalen*, 1905, **341**, 80—98. Compare preceding abstract).—When the sodium salt of β-benzylidenelævulic acid is treated with ethyl sodiomalonate, a hydroresorcinol derivative, *carbethoxyphenylhydroresorcinylacetic acid*, $\begin{matrix} CH(CO_2Et)\cdot CHPh \\ | \\ CO——CH{:}C(OH) \end{matrix}\!\!>\!CH\cdot CH_2\cdot CO_2H$, is formed. The acid crystallises from boiling water in aggregates melting at 167°, and from dilute alcohol in rhombohedra melting at 156°; with alcoholic ferric chloride it gives a violet coloration. Methyl sodiomalonate yields an analogous acid, $C_{16}H_{16}O_6$, which crystallises in leaflets melting at 172—173°; the sodium salt, $C_{16}H_{14}O_6Na_2$, was prepared.

From δ-benzylidenelævulic acid and ethyl sodiomalonate, the isomeric acid, $\begin{matrix} CHPh\cdot CH_2\cdot C(OH) \\ | \\ CH(CO_2Et)——CO \end{matrix}\!\!>\!C\cdot CH_2\cdot CO_2H$, is obtained, crystallising from water in needles with H_2O, melting at about 123°; when heated at 100°, it loses water and then melts at 143°.

Addition does not take place between sodium benzylidenemalonate and ethyl sodiomalonate. The *monoethyl* ester of benzylidenemalonic acid, $CHPh{:}C(CO_2Et)\cdot CO_2H$, is formed by heating an acetic acid solution of potassium ethyl malonate and benzaldehyde, and crystallises in prismatic plates melting at 85°. It forms an additive compound with ethyl sodiomalonate, but not with sodium ethoxide.

Ethyl cinnamate forms an additive product with potassium ethyl malonate in the presence of sodium ethoxide, but not with sodium malonate under the same conditions.

Cinnamoyl-o-aminobenzoic acid, $CHPh{:}CH\cdot CO\cdot NH\cdot C_6H_4\cdot CO_2H$, prepared by heating cinnamoyl chloride and anthranilic acid, forms crystals melting at 192°; at the same time, a neutral *compound* crystal-

lising in needles and melting and decomposing at 226—228° is produced. *Cinnamoyl*-m-*aminobenzoic acid* forms rhombohedra melting at 253°, and the corresponding p-*acid* crystals melting and decomposing at 282°. An additive product with ethyl sodiomalonate is only obtained from the ortho-acid. K. J. P. O.

Fluorescein and the Non-existence of β-*p*-Dibromodinitrobenzene. GUSTAV HELLER and HEINRICH L. MEYER (*J. pr. Chem.*, 1905, [ii], **72**, 197—200. Compare Heller, Abstr., 1895, i, 234; Meyer, *ibid.*, i, 538).—That only one dihydroxybenzoylbenzoic and one dibromodihydroxybenzoylbenzoic acid are obtained from fluorescein and eosin respectively shows both hydroxyl groups in these substances to occupy the para-position.

The authors have been able to isolate only α- and γ-*p*-dibromodinitrobenzenes from the product obtained on nitration of *p*-dibromobenzene. The part of the product which should have contained Austen's β-*p*-dibromodinitrobenzene (this Journal, 1876, ii, 406, 513) yielded, on reduction, *p*-dibromo-*o*-diamino- and *p*-dibromo-*p*-diamino-benzene together with a small amount of a substance which was probably *m*-dibromoaniline. Austen's substance may have been γ-compound.

G. Y.

Meconic Acid. L. VALENTI (*Chem. Centr.*, 1905, ii, 491; from *Boll. Chim. Farm.*, 1905, **44**, 373—380).—Meconic acid is extracted from powdered opium by evaporating it to dryness with dilute hydrochloric acid, extracting with absolute alcohol, and making the filtrate alkaline by means of alcoholic potash; the precipitate so formed is washed with a mixture of equal parts of alcohol and ether, dissolved in water, and treated with lead acetate; the precipitated lead salt after washing is decomposed with hydrogen sulphide, the solution being boiled, filtered, and cooled. One part of pure meconic acid dissolves in 50 parts of methyl alcohol or ethyl acetate, and in 100 parts of water or acetone; it is soluble in alcohol or benzene, very slightly so in amyl alcohol, light petroleum, carbon disulphide, or glycerol. A number of colour reactions are described which may be obtained under suitable conditions from meconic acid by the action of potassium persulphate, iodic acid, concentrated nitric acid, followed by potassium hydroxide, sodium metavanadate, ammonium molybdate, and ferric chloride. A full account is also given of the precipitation reactions obtained by the addition of albumin, the nitrates of mercury and silver, and by lead acetate and the salts of cobalt, nickel, and gold. Papaverine hydrochloride and quinine sulphate both give white precipitates with ammonium meconate. Apomorphine hydrochloride produces at first a white and then a blue precipitate, and strychnine sulphate gives after some time a crystalline precipitate. Meconic acid reduces potassium dichromate and permanganate in cold acid solution, and potassium ferrocyanide on heating, with the production of a blue coloration.

The salts of meconic acid are prepared by mixing alcoholic solutions of the acid and of the acetate of the corresponding metal, if necessary adding ether to ensure complete precipitation. Meconic acid, $C_5H(OH)_2(CO_2H)_2O_2,3H_2O$, may be titrated with $N/10$ potassium

hydroxide until the appearance of a yellow colour, which indicates the formation of a basic salt by replacement of a phenolic hydroxyl, the normal salts being colourless. Meconic acid and its salts are not poisonous, although they combine with proteids. Meconic acid can always be detected in toxicological cases by adding ferric chloride to the dried organs after treatment with hydrochloric acid. P. H.

Compounds from Lichens. XIV. Wilhelm Zopf (*Annalen*, 1905, **340**, 276—309. Compare Abstr., 1904, i, 1020; this vol., i, 212).—Sphærophorin, sphærophoric acid, fragilin, and a small amount of a violet substance have been obtained from a specimen of *Sphærophorus fragilis* from the Tafelsteinkuppe, near Wolfshan, in the Riesengebirg (compare Abstr., 1898, i, 489). Sphærophorin, $(C_{14}H_{16}O_4)_n$ or $C_{28}H_{34}O_8$, crystallises from benzene in long, slender, white needles, is soluble in ether, and reduces potassium permanganate in cold sodium carbonate solution. Sphærophoric acid crystallises from ether in large, rhombic plates, from glacial acetic acid in thin leaflets resembling thamnolic and squamatic acids, melts and decomposes at 206—207°, and dissolves in aqueous alkali hydroxides or carbonates to form yellow solutions, which become slowly red or violet, and on addition of hydrochloric acid yield a yellow *resin* and a colourless substance crystallising in sheaves of needles. The acid reddens alcoholic litmus, gives a violet coloration with traces of ferric chloride, reduces potassium permanganate in cold sodium carbonate solution, and dissolves in concentrated sulphuric acid to form a colourless solution, which on warming becomes red, brown, and finally black. With baryta water, sphærophoric acid forms a colourless *substance*, which crystallises in stellate aggregates of long, slender, feathery needles. Fragilin crystallises in rosettes of rectangular plates, is green by transmitted light, and is insoluble in cold aqueous sodium carbonate, but dissolves when warmed to form a reddish-violet solution.

Biatora mollis (*Lecidea mollis*) contains 4·5 per cent. of diffusin (Abstr., 1899, i, 716; 1903, i, 762), which is now termed *diffusic acid*. This gives a violet coloration with ferric chloride, and when boiled with dilute potassium hydroxide forms a substance which gives a red coloration with bleaching powder, and red with green fluorescence on addition of a drop of chloroform. The *sodium* and *barium* salts are described.

Rhizocarpic acid has been found in a sterile specimen of *Biatora lucida* obtained from schist in the Brilonwald, in Sauerland. This acid was mistaken by Knop (*Annalen*, 1844, **49**, 122) for usnic acid.

Umbilicaric acid, lecanoric acid, and a substance which may be gyrophoric acid were obtained from *Gyrophora polyrrhiza*.

Contrary to Hesse's statement (Abstr., 1903, i, 706), *Lepraria latebrarum* contains neither usnic nor talebraric acids. The appearance of hydroxyroccellic acid (Hesse, *loc. cit.*) must have been due to oxidation of the roccellic acid during the recrystallisation from boiling glacial acetic acid.

Rhizoplaca opaca (*Lecanora chrysoleuca β-opaca*, *Parmelia rubina β-opaca*, *Squamaria chrysoleuca β-opaca*), gathered from gneiss blocks

near Sölden, in the Oetzthal, in Tyrol, contains usnic, placodiolic, and rhizoplacic acids.

Placodiolic acid, previously termed placodiolin (Abstr., 1898, i, 90), is soluble in aqueous sodium hydrogen carbonate, and is reprecipitated by hydrochloric acid.

Rhizoplacic acid, $C_{21}H_{40}O_5$, crystallises in white, tetragonal leaflets, melts at 94—95°, and is soluble in warm ether, hot alcohol, chloroform, benzene, glacial acetic acid, or aqueous alkali hydroxides or carbonates; the solution in aqueous potassium hydroxide forms a lather. In concentrated sulphuric acid, the acid dissolves to form a lemon-yellow solution which, on exposure to air, deposits the unchanged white substance.

Usnea microcarpa, from South Tyrol, contains 3·3 per cent. of *d*-usnic and 0·1 per cent. of usnaric acid. Salazinic acid, from *Parmelia conspersa*, has been converted by boiling acetic anhydride into salazinaric acid melting at 206—207° (compare Hesse, *loc. cit.*).

Gasparrinia sympagea contains parietin.

Theloschistes flavicans contains parietin and a colourless *substance*, which crystallises in spherical aggregates of thin leaflets, melts at 240—245°, and is insoluble in aqueous alkali hydroxides or concentrated sulphuric acid.

Ochrolechia androgyna (*Lecanora subtartarea*) contains gyrophoric acid, calyciarin, and a small amount of a *substance* which crystallises in thick, colourless prisms.

l-Usnic acid, a *substance* which forms colourless, slender crystals and is insoluble in alcohol or chloroform, and a crystalline *acid* which is easily soluble in alcohol and moderately so in glacial acetic acid and aqueous sodium hydrogen carbonate, from which it is reprecipitated on addition of hydrochloric acid, were isolated from *Cladonia incrassata*, obtained from Wildenloh in Oldenburg. The occurrence of ramalic acid (Hesse, this vol., i, 138), which may be identical with protocetraric acid, in *Ramalina farinacea* is confirmed. The purplish-violet coloration shown by *Physcia endococcina* when treated with potassium hydroxide is due to the presence of the two anthracene colouring matters, rhodophyscin, which is red, crystallises in small leaflets, and decomposes above 260°, and endococcin, which crystallises in yellow prisms. The lichen contains also atranoric acid and zeorin. G. Y.

m-Halogen-benzaldehydes. Carl Mettler (*Ber.*, 1905, **38**, 2809—2812).—*m*-Halogen-benzaldehydes are prepared by electrolytic reduction of the corresponding halogen-benzoic acids to the halogen-benzyl alcohols (this vol., i, 436), and oxidation of these with nitric acid in sulphuric acid solution at 40—50°.

m-Bromobenzaldehyde prepared by this method boils at 228—230° under 726 mm. pressure (compare Baeyer and Wirth, Abstr., 1895, i, 288). A specimen prepared by Einhorn and Gernsheim's method (Abstr., 1895, i, 281) boiled at 224—226° under 726 mm. pressure. The phenylhydrazone melts at 143—144°; the oxime melts at 73°.

β-Hydroxy-*β*-5-chloro-2-nitrophenylethyl methyl ketone melting at 106° is prepared by the condensation of 5-chloro-2-nitrobenzaldehyde with acetone in presence of trisodium phosphate. G. Y.

Thiele's Xylene-oxidation and Terephthalaldehyde-green. Paul Claussner (*Ber.*, 1905, 38, 2860—2862).—The oxidation of *p*-xylene by means of a mixture of acetic anhydride and sulphuric acid (Thiele and Winter, Abstr., 1900, i, 500) leads to the formation of terephthalaldehyde tetra-acetate and *p*-tolualdehyde diacetate; the former is the principal product if the reaction is carried out at 10—18°, the latter, if at $-2°$ to $-10°$. p-*Tolualdehyde diacetate*, $C_7H_7 \cdot CH(OAc)_2$, is formed also by the action of acetic anhydride on *p*-tolualdehyde at 150—180°; it crystallises in colourless, glistening leaflets, melts at 69°, is soluble in cold alcohol, but insoluble in aqueous alkali hydroxides, and forms a leuco-malachite-green when heated with dimethylaniline and zinc chloride.

Octamethyltetraminotetraphenyl-p-*xylene*, $C_6H_4[CH(C_6H_4 \cdot NMe_2)_2]_2$, is formed by the condensation of terephthalaldehyde tetra-acetate and dimethylaniline in presence of zinc chloride; it forms a crystalline powder, melts and decomposes at 243—248°, is easily soluble in benzene or dilute acetic acid, but is insoluble in water, alcohol, or ether, and, on oxidation with lead peroxide in acetic acid solution, yields *terephthalaldehyde-green*, which closely resembles malachite-green. G. Y.

Decomposition of the Sodium Derivative of *iso*Nitrosoacetophenone. C. H. Sluiter (*Rec. Trav. chim.*, 1905, [ii], 24, 365—367).—The sodium derivative of *iso*nitrosoacetophenone is coloured, and on heating in aqueous solution is decomposed according to the equation $COPh \cdot CH \colon NONa = Ph \cdot CO_2Na + HCN$; a determination of the velocity of this reaction, using a colorimetric process, shows it to be unimolecular; the velocity-coefficient, which is independent of the concentration for values between 1 and 5 per cent., increases with the temperature, and diminishes on the addition of a small quantity ($\frac{1}{2}$ mol.) of sodium hydroxide, becoming normal again as the quantity is increased to 10 mols. In alcoholic solution, the velocity-coefficient is also diminished, the diminution being less in the case of methyl than of ethyl alcohol. M. A. W.

Properties of β-Anilinoketones derived from Fatty Ketones. Charles Mayer (*Bull. Soc. chim.*, 1905, [iii], 33, 958—961. Compare this vol., i, 214, 357).—β-Anilinoketones of the constitution

$$NHR' \cdot CHPh \cdot CH_2 \cdot CO \cdot R,$$

where R is an alkyl, R′ a phenyl or substituted phenyl group, are decomposed by the action of concentrated acids, acid chlorides, phenylcarbimide, or of piperidine, forming the unsaturated ketone,

$$CHPh \colon CH \cdot CO \cdot R,$$

and the corresponding aniline, anilide, or phenylcarbamide. On the other hand, the action of phenylhydrazine or semicarbazide hydrochloride, or of ethyl acetoacetate in presence of piperidine, leads to the decomposition of the β-anilinoketone into its generators: the fatty ketone, the aniline, and benzaldehyde, which is obtained as the phenylhydrazone or semicarbazone, or as ethyl benzylidenebisacetoacetate. G. Y.

Addition of Acids and Salts to $\alpha\beta$-Unsaturated Ketones. DANIEL VORLÄNDER (*Annalen*, 1905, **341**, 1—80. Compare Abstr., 1903, i, 495, 632; 1904, i, 65).—The author's theory as to the formation of additive products of acids, salts, or the halogens with unsaturated ketones is discussed in the light of earlier experiments (*loc. cit.*) and of his later work. Two series of additive products are formed; the coloured unstable additive products, type A, have a very great velocity of formation, whilst that of the colourless, stable products, type B, is easily measurable.

[With C. SIEBERT.]—Molecular proportions of aldehydes and acids readily combine, as has been previously observed, the additive product belonging to type A but being only faintly coloured. At lower temperatures, these derivatives of aromatic aldehydes combine with a second molecule of halogen acid. The constitution of these additive products is regarded as analogous with that of the cyanohydrins. Hydrogen bromide and benzaldehyde yield at the ordinary temperature benzylidene bromide, but hydrogen chloride does not give the corresponding chloride.

Benzaldehyde monohydrobromide, CHBrPh·OH, is formed at $-19°$ as colourless crystals or leaflets, loses hydrogen bromide rapidly on exposure to the air, and is decomposed by water. *Anisaldehyde monohydrochloride*, $OMe·C_6H_4·CHO,HCl$, formed at the ordinary temperature, crystallises in needles; at from $-15°$ to $-75°$, the *dihydrochloride* is produced and forms a grey mass. The *monohydrobromide* is formed in acetic acid or petroleum solution, and crystallises in colourless needles. *Piperonal monohydrochloride*, $C_8H_6O_3,HCl$, is obtained from $-15°$ to the ordinary temperature; the *dihydrochloride* is formed at $-75°$; both are yellow; the *monohydrobromide* forms yellow, prismatic crystals. No definite substance is formed from vanillin.

Chloral monohydrochloride, $CCl_3·CHO,HCl$, is a white, crystalline mass, and at $-75°$ takes up no more hydrogen chloride. The polymerides, meta- and para-chloral, do not combine with hydrogen chloride. *Chloral monohydrobromide*, $CCl_3·CHO,HBr$, is a white, crystalline powder. *Bromal monohydrobromide* was obtained.

The temperature interval in which the additive products of the ketones are formed is lower and more limited than that of the other carbonyl derivatives. Many mono- and di-ketones react at the ordinary temperature with the hydrogen haloids, but not at 0°. The following substances form additive products at $-75°$: benzophenone, acetophenone, deoxybenzoin, benzil, anthraquinone, and phenanthraquinone; benzil does not form an additive product above $-18°$, and benzophenone not at $-12°$, but at $-17°$. Benzoin, anthraquinone, alizarin, and phenanthraquinone do not form compounds above $-18°$; benzylacetone and benzylacetophenone react from $-15°$ to $-18°$, and form several additive products according to the length of the treatment with the acid.

Phenolethylene derivatives form intensely coloured additive products of type A. It follows, therefore, that the carbonyl oxygen of unsaturated ketones is not essential for the development of colour. The colour would rather appear to be dependent on an interaction of the acid with the ethylene linking, and possibly the aromatic nucleus.

Anethole, *iso*safrole, *iso*apiole, *iso*methyleugenole, and asarone give such coloured additive products, but they cannot be isolated. A liquid *compound* is obtained from benzene at $-75°$, which contains three mols. (?) of hydrogen chloride. Unsaturated hydrocarbons do not yield additive products. Anisylideneacetophenone yields a *dipicrate*, $C_{16}H_{14}O_2,2C_6H_3O_7N_3$, which crystallises in orange-coloured needles melting at about 87°. *Piperonalacetophenone dipicrate*,

$$C_{16}H_{12}O_3,2C_6H_3O_7N_3,$$

crystallises in orange needles melting at 126—128°. *Cinnamylideneacetophenone dipicrate*, $C_{17}H_{14}O,2C_6H_3O_7N_3$, crystallises in yellow needles melting at 115—117°. *Benzylideneacetophenone dipicrate*, $C_{15}H_{12}O,2C_6H_3O_7N_3$, crystallises in pale yellow needles melting at 93—97°. *Anisylidenepinacolin dipicrate*, $C_{14}H_{18}O_2,2C_6H_3O_7N_3$, crystallises in yellow needles melting at 157—159°. *Dipiperonylideneacetone monopicrate* crystallises in red needles melting at 151—153°. *Anisylidene* and *piperonylidenepinacolin* were prepared in the same manner as benzylidenepinacolin ; the former melts at 34° after distillation under reduced pressure, and the latter crystallises from petroleum in needles melting at 96°.

[With O. Rolle.]—Anisylideneacetophenone forms a *dihydrochloride*, type A, $C_{16}H_{14}O_2,2HCl$, crystallising in dark red needles or flattened prisms ; when kept in petroleum saturated with hydrogen chloride, it is transformed into the *monohydrochloride*, type B, crystallising in colourless plates or leaflets, melting and decomposing at 86—88° and easily decomposed by water. The following substances yield additive products with hydrogen chloride, which were not isolated in a pure state : piperonylideneacetophenone, dipiperonylideneacetone, methyl *p*-methoxycinnamate, and *p*-hydroxybenzylideneacetophenone ; similar compounds with hydrogen bromide were obtained from anisylideneacetophenone, *p*-hydroxybenzylideneacetophenone, and methyl *p*-methoxycinnamate.

The *hydrochloride*, type B, of benzylideneacetophenone condenses with benzaldehyde when the mixture is saturated with hydrogen chloride, forming a *compound*, $COPh\cdot CH(CHPhCl)_2$; it crystallises in white needles from methyl alcohol and melts at 155°.

[With C. Siebert.]—The additive products formed by the action of bromine on solutions of aromatic ketones belong to type B. The coloured additive products of type A are apparently formed under certain conditions, as by the action of bromine vapour on solid dry dibenzylideneacetone. When dibenzylideneacetone is brominated, substances are formed containing bromine, besides the known tetrabromide. Dicinnamylideneacetone forms an *octobromide*, $C_{21}H_{18}OBr_8$, which crystallises in needles melting and decomposing at 200—202°.

Diphenyldimethyltetrahydropyrone and the so-called dibenzylidenediethyl ketone, $C_{19}H_{18}O$ (shown by Japp and Maitland, Trans., 1904, **85**, 1473, to be dimethyl*cyclo*pentanone), show an abnormal behaviour towards sulphuric acid, in that the former, which does not possess an ethylene linking, gives a yellow coloration with sulphuric acid, whilst the latter, which as an unsaturated ketone does possess an ethylene linking, yields no such coloration. Dimethyl*cyclo*pentanone yields, on oxidation with chromic and sulphuric acids, an *acid*, $C_{17}H_{14}O_3$,

of unknown constitution, which crystallises in colourless needles melting at 175°. The *silver* salt, $C_{17}H_{13}O_3Ag$, was prepared. The *ethyl* ester, $C_{17}H_{13}O_2$,OEt, melts at 118—120°, and the *methyl* ester at 73°.

Addition of Ethyl Sodiomalonate to the Sodium Salts of Unsaturated Acids.—The mechanism of the reaction is discussed at considerable length. Ethyl sodiomalonate shows a greater tendency to form additive products with the esters of α-unsaturated acids than with the sodium salts. Thus the sodium salts of crotonic, sorbic, cinnamenylacrylic, cinnamic, phenyl-$\beta\gamma$-crotonic, and benzylidenemalonic acids do not combine with ethyl sodiomalonate, whilst their esters react easily. On the other hand, since the sodium salts of the β- and δ-benzylidenelævulic acid and of cinnamoylanthranilic acid react, it would appear that the saline properties do not prevent the addition. The esters of the hydroresorcinols and the sodium salts of the diketones do not react with the sodiomalonate; a similar inactivity is observed in the case of the sodium salts of *p*-hydroxybenzylideneacetophenone and the ester of *p*-coumaric acid. The disodium salt and the salt of the mono-ethyl ester of malonic acid do not react in the same way with the unsaturated ketones and esters as does the di-ethyl ester. The presence of acids prevents the interaction both of ethyl malonate and of malonic acid with cinnamic acid.

Ethyl malonate does not interact either with unsaturated esters or ketones possessing one carbonyl group. Since ethyl sodiomalonate in alcoholic solution reacts with such substances, it would appear that the presence of sodium ethoxide favours the addition by the formation of additive products. In certain cases, these intermediate additive products can be isolated, but it is found that they are less reactive than the unsaturated ester itself. The formation of such products is entirely prevented when the reaction of the unsaturated ester and the ethyl sodiomalonate is carried out in the presence of ethyl malonate as solvent. It would seem from these experiments that a direct addition of the sodiomalonate to the unsaturated ester is the starting-point of the greater number of these reactions.

[With Paul Weissheimer.]—The additive products which are formed from ethyl sodiomalonate and dimethylpyrone belong to type A, since they are decomposed by solvents and show the reactions of the components. The molecular additive *product*, $C_{14}H_{19}O_6Na$, is formed in benzene or ethereal solution, and crystallises in slender, colourless needles. The *compound*, $C_{15}H_{21}O_6Na$, of dimethylpyrone and ethyl sodiomethylmalonate crystallises in hexagonal leaflets or prisms. The *compound*, $C_{12}H_{15}O_6Na$, of dimethylpyrone and methyl sodiomalonate crystallises from benzene in needles.

Amines form two classes of additive products. The compounds of tertiary amines with alkyl haloids belong to type B, whereas the acid compounds of amines are classed under type A. Observation would show that two distinct processes occur in the addition of acids to amines, differing in the energy transformations which accompany the reaction. The observations of earlier investigators are discussed, and the influence of water and other solvents on the formation of these additive compounds is considered from this point of view.

In the addition of two salts, a far more complicated process is observed than in the case of amines. It is thought that double salts are additive compounds of the type A, whilst complex salts belong to type B. K. J. P. O.

Reactions of *iso*Amylanthrone Chloride and Bromide. E. Jüngermann (*Ber.*, 1905, **38**, 2868—2873. Compare Liebermann and Lindenbaum, this vol., i, 522).—9-iso*Amylanthrone bromide*,

$$CO<{}^{C_6H_4}_{C_6H_4}>CBr\cdot C_5H_{11},$$

is formed by the action of hydrogen bromide on *iso*amyloxanthranol in benzene solution; it crystallises in white rhombohedra and melts at 97—98°. 9-*Ethoxy*-9-iso*amyl*-10-*anthrone*, $CO<{}^{C_6H_4}_{C_6H_4}>C(C_5H_{11})\cdot OEt$, prepared by boiling *iso*amylanthrone chloride in ethyl alcohol in a reflux apparatus, crystallises in colourless prisms, melts at 53°, deliquesces in contact with organic solvents, and when treated with hot concentrated sulphuric acid forms a red coloration and the intramolecular condensation product, $C_{19}H_{14}O$, melting at 206° (Liebermann and Landshoff, Abstr., 1882, 608). 9-*Methoxy*-9-iso*amyl*-10-*anthrone*, $C_{20}H_{22}O_2$, forms colourless crystals and melts at 67—69°. 9 : 10-*Diphenoxy*-9 : 10-iso*amylenedihydroanthracene*, $OPh\cdot C\begin{matrix}\diagup C_6H_4-\diagdown \\ -C_5H_{10}- \\ \diagdown C_6H_4-\diagup\end{matrix}C\cdot OPh$, formed when *iso*amylanthrone chloride is boiled with phenol (2 mols.) in benzene solution in a reflux apparatus, crystallises in yellow needles, melts at 67—71°, is easily soluble in all organic solvents, but is insoluble in aqueous alkali hydroxides, does not form an acetyl derivative, and when treated with hot concentrated sulphuric acid yields the intramolecular condensation product, $C_{19}H_{14}O$.

9-*Hydroxyphenyl*-9-iso*amyl*-10-*anthrone*,

$$CO<{}^{C_6H_4}_{C_6H_4}>C(C_5H_{11})\cdot C_6H_4\cdot OH,$$

is formed by the action of phenol (1 mol.) on *iso*amylanthrone chloride in cold glacial acetic acid solution; it crystallises in colourless prisms, melts at 228°, and is moderately soluble in dilute potassium hydroxide. The *acetyl* derivative, $C_{25}H_{23}O_2Ac$, crystallises in colourless needles and melts at 148—150°.

9-*Dihydroxyphenyl*-9-iso*amyl*-10-*anthrone*,

$$CO<{}^{C_6H_4}_{C_6H_4}>C(C_5H_{11})\cdot C_6H_3(OH)_2,$$

formed from resorcinol and *iso*amylanthrone chloride, crystallises in colourless prisms, melts at 262°, and is easily soluble in dilute potassium hydroxide. The *diacetyl* derivative, $C_{29}H_{28}O_5$, crystallises in colourless needles and melts at 161°.

9-*Phenyl*-9-iso*amyl*-10-*anthrone*, $CO<{}^{C_6H_4}_{C_6H_4}>CPh\cdot C_5H_{11}$, is formed by the action of aluminium chloride on *iso*amylanthrone chloride in benzene solution; it crystallises in colourless prisms and melts at 139°. When heated with hydriodic acid and red phosphorus in a reflux

apparatus, it forms 9-*phenyl*-9-iso*amyldihydroanthracene*,

$$CH_2{<}{}^{C_6H_4}_{C_6H_4}{>}CPh{\cdot}C_5H_{11},$$

which separates from alcohol in colourless crystals, melts at 85°, is easily soluble in all organic solvents, and when treated with bromine in carbon disulphide solution yields 10-*bromo*-9-*phenyl*-9-iso*amyldihydroanthracene*, $CHBr{<}{}^{C_6H_4}_{C_6H_4}{>}CPh{\cdot}C_5H_{11}$. This separates from light petroleum in colourless crystals and melts at 134—137°.

9 : 10-*Dihydroxy*-9 : 10-*di*iso*amyldihydroanthracene*,

$$OH{\cdot}C(C_5H_{11}){<}{}^{C_6H_4}_{C_6H_4}{>}C(C_5H_{11}){\cdot}OH,$$

formed by the action of magnesium *iso*amyl bromide on *iso*amyloxanthranol in ethereal solution, separates on evaporation of its ethereal solution in colourless crystals, melts at 170—174°, dissolves easily in benzene, more sparingly in alcohol or light petroleum, to form solutions with blue fluorescence, and gives a red coloration with hot concentrated sulphuric acid. On addition of concentrated sulphuric acid to its solution in glacial acetic acid, it yields 9 : 10-*diamylenedihydroanthracene*, $C_5H_{10}{:}C{<}{}^{C_6H_4}_{C_6H_4}{>}C{:}C_5H_{10}$, which crystallises in yellow prisms, melts at 103—108°, dissolves in all organic solvents to form solutions with blue fluorescence, and decolorises bromine (2 mols.) in carbon disulphide solution with evolution of hydrogen bromide. When boiled for 5—10 minutes with hydriodic acid of sp. gr. 1·96, it is reduced to 9 : 10-*di*iso*amylanthracene*, $C_5H_{11}{\cdot}C{\lessdot}{}^{C_6H_4}_{C_6H_4}{\gtrdot}C{\cdot}C_5H_{11}$, which crystallises in yellowish-green needles, melts at 132—137°, is easily soluble in organic solvents, and is not reduced when boiled with hydriodic acid and red phosphorus for three hours. G. Y.

Wislicenus's Supposed Isomeride of Dibenzoylmethane. C. H. Sluiter (*Rec. Trav. chim.*, 1905, [ii], **24**, 368—371).—Independently of Ruhemann and Watson (Trans., 1904, **85**, 456), the author has proved that the compound described by Wislicenus as an isomeride of dibenzoylmethane (Abstr., 1900, i, 37) is α-ethoxybenzylideneacetophenone, OEt·CPh:CH·COPh. The compound appears to exist in two stereoisomeric forms, $\begin{matrix}COPh{\cdot}C{\cdot}H\\ \| \\ OEt{\cdot}C{\cdot}Ph\end{matrix}$ and $\begin{matrix}COPh{\cdot}C{\cdot}H\\ \| \\ Ph{\cdot}C{\cdot}OEt\end{matrix}$, for when first prepared it melts at 61°; the melting point slowly changes until after some months it becomes constant at 77°. An attempt to prepare α-ethoxybenzylideneacetophenone by the action of ethyl iodide on the sodium derivative of dibenzoylmethane resulted in the formation of αα-dibenzoylpropane, $CHEt(COPh)_2$ (compare Auger, *Ann. Chim. Phys.*, 1891, [vi], **22**, 348). α-*Methoxybenzylideneacetophenone*,

OMe·CPh:CH·COPh,

prepared by the action of sodium methoxide on bromobenzylideneacetophenone, is a yellow oil boiling at 220—222° under 16 mm. pressure, and solidifying in a mixture of solid carbon dioxide and alcohol to crystals which melt at −11°. M. A. W.

Action of Mercaptides on Quinones. JOHN L. SAMMIS (*J. Amer. Chem. Soc.*, 1905, **27**, 1120—1127).—An improved method is described for the preparation of tetraethylthiolquinone, first obtained by Grindley and Sammis (Abstr., 1897, i, 403), by means of which a yield amounting to 95 per cent. of the theoretical can be obtained.

When an alcoholic solution of lead acetate is added to a solution of tetraethylthiolquinol, a *compound*, $C_6(SEt)_4(OPb{\cdot}OAc)_2$, is obtained as a yellow, crystalline precipitate; the formation of this lead salt serves as a delicate test for tetraethylthiolquinol.

The substance described as tetraethylthiolquinonedibenzoyldithiobenzoylacetal (*loc. cit.*) is now found to be *tetraethylthiolquinol dibenzoate*, $C_6(SEt)_4(OBz)_2$.

When a solution of sodium ethoxide is added to tetraethylthiolquinone moistened with a little alcohol, *diethylthioldiethoxyquinol dibenzoate*, $C_6(SEt)_2(OEt)_2(OBz)_2$, is obtained, which crystallises in equilateral, six-sided plates, melts at 184—184·5°, and is soluble in benzene, chloroform, or ether.

The results of this investigation have shown that the action of mercaptides on quinones is a process of substitution and reduction, no additive products having yet been isolated. E. G.

[1:4-Dibromo-2-aminoanthraquinone.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 158474).—Bromination of β-aminoanthraquinone in aqueous suspension or in indifferent solvents with a slight excess of bromine yields 1:4-*dibromo-2-aminoanthraquinone*, which crystallises in orange needles, melts at 239—240°, and dissolves in acetic acid, nitrobenzene, pyridine, hot alcohol, or concentrated sulphuric acid to yellow solutions. When heated with sodium acetate and metallic salts (this vol., i, 720), it yields an *azine*,

$$C_6H_4{<}^{CO}_{CO}{>}C_6HBr{<}^{NH}_{NH}{>}C_6HBr{<}^{CO}_{CO}{>}C_6H_4,$$

dissolving in hot nitrobenzene or aniline to a greenish-blue solution. Water precipitates the azine in blue flocks from its olive-brown solution in concentrated sulphuric acid. A fast greenish-blue dye is obtained on reducing it in alkaline solution. C. H. D.

Aryl Ethers of Anthraquinone Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 158531).—The aryl ethers of anthraquinone derivatives may be prepared by heating halogen, nitro-, or sulpho-derivatives of anthraquinone with alkali phenoxides, the negative group being replaced by the phenol residue.

Erythroxyanthraquinone phenyl ether (1-*phenoxyanthraquinone*), prepared by heating 1-bromo- or 1-nitro-anthraquinone or potassium anthraquinone-1-sulphonate with potassium phenoxide at 170°, crystallises from ethyl acetate in radiating groups of yellow prisms and melts at 145°. 1:5-*Diphenoxyanthraquinone* separates from acetic acid or nitrobenzene in long, yellow needles and melts at 215°.

1:5-*Di-β-naphthoxyanthraquinone*, from 1:5-dinitroanthraquinone and potassium β-naphthoxide, crystallises from acetic acid in bright yellow needles and melts at 243—245°. 1:5-*Di*-o-*tolyloxyanthraquinone* forms golden leaflets and melts at 190°; the p-*tolyl ether* forms long,

yellow needles and melts at 223—225°. 2-*Phenoxyanthraquinone* melts at 153°, *chrysazin diphenyl ether* melts at 189—190°.

It is also possible to replace one of several negative groups present in the molecule. Thus 1-nitroanthraquinone-6-sulphonic acid and potassium phenoxide yield 1-*phenoxyanthraquinone*-6-*sulphonic acid*, the *ammonium* salt of which forms glistening, yellow leaflets. 1-*Anilino*-5-*phenoxyanthraquinone*, from 5-nitro-1-anilinoanthraquinone, forms red, glistening needles and melts at 188—190°.

The preparation of other similar derivatives is described.

C. H. D.

Stereoisomeric Menthols. IWAN KONDAKOFF (*J. pr. Chem.*, 1905, [ii], **72**, 185—193).—It has been held by various authors that *d*-menthol forms an intermediate stage in the conversion of *l*-menthol into *tert.*-menthol or its derivatives. Contrary to this view is the formation of Δ^3- and not Δ^2-menthene from *l*-menthol, and the fact that *d*-menthol is more stable than is generally assumed.

The ethereal oil of Bucco leaves (Abstr., 1897, i, 227) is now found to contain (1) dipentene and limonene, (2) a ketone which boils at 86° under 10 mm. pressure and has $[\alpha]_D$ −51°, and (3) a mixture of diosphenol with a compound of diosphenol and an acid melting at 94°. The ketone, which is more easily obtained from *Barosma serratifolia*, forms a glistening, crystalline *hydrazone* melting at 80° and two *semicarbazones*, of which the one only slightly soluble in alcohol melts at 180°, whilst the other, more soluble, melts at 123°. On treatment of the former semicarbazone with sulphuric acid there is obtained an inverted ketone, which boils at 85·5—86° under 10 mm. pressure, has a sp. gr. 0·897 at 19·5°, $[\alpha]_D$ −22·3°, n_D 1·45169, and on reduction with sodium in methyl-alcoholic solution yields *d*-menthol. This yields *d*-menthene and forms haloid esters consisting of a mixture of unstable derivatives of *tert.*-menthol and stable dextrorotatory derivatives of *d*-menthol.

On reduction by Leuckart's method, *d*-menthone yields d-*formylmenthylamine*, melting at 117—118° and having $[\alpha]_D$ +154·47°, together with a small amount of the *l*-amine. *d*-*iso*Menthol, obtained from *d*-menthylamine or together with *d*-menthol on reduction of *l*- or *d*-menthone, boils at 83·5—84°, has $[\alpha]_D$ +25·64°, and on oxidation yields *d*-menthone. The corresponding *l*-*iso*menthol is unknown.

Brünel's *i*-menthol (this vol., i, 197), melting at 29—31°, is probably identical with Richtmann and Kremer's substance (Abstr., 1897, i, 84). A second *i*-menthol is described by Beckmann (Abstr., 1897, i, 248).

The properties of the *i*-menthol described by Baehr (*Synthese eines inactiven menthens*, Leipzig, 1898) resemble those of *tert.*-menthol, but it may be a new secondary *i*-menthol if Hagemann's acid is a δ-keto-, and not a β-keto- or mixture of β- and δ-keto-acids (Merling, this vol., i, 349). *tert.*-Menthol is optically inactive, does not form a urethane, and when treated with carbanil loses water, forming a menthene which boils at 170—175° and has a sp. gr. 0·812 at 20°/4° and n_D 1·45627. *tert.*-Menthol forms a liquid, but not a solid, *nitrosochloride*. This boils at 128—152° under 11 mm. pressure, or, after

treatment with hydrogen chloride in ethereal solution, at 128—140°, distils in a current of steam without appreciable decomposition, and loses hydrogen chloride when treated with sodium ethoxide, acetates in acetic acid solution, or alcoholic potassium hydroxide, forming nitrosomenthene.

Reduction of diosphenol leads to the formation of a liquid *i*-menthol, which boils at 98—100·5° under 12 mm. or at 214·5—216° under 759 mm. pressure, has a sp. gr. 0·9052 at 20° and n_D 1·464456, and may be identical with Brünel's α-thymomenthol (*loc. cit.*). It forms an inactive iodide which yields an *i*-menthene boiling at 168—169°, and having a sp. gr. 0·8264 at 19·8°/4°. G. Y.

Condensation Compounds of Camphoroxalic Acid and Amines. J. Bishop Tingle and William E. Hoffman, jun. (*Amer. Chem. J.*, 1905, **34**, 217—254. Compare Trans., 1890, **57**, 652; Abstr., 1897, i, 484; 1898, i, 443; 1899, i, 444; 1900, i, 302; 1901, i, 632).—*Copper, silver, barium, calcium*, and *ferric camphoroxalates* are described.

The action of amines on camphoroxalic acid has been studied. With β-naphthylamine, *β-naphthylamine β-naphthylcamphoformeneaminecarboxylate* is produced, which melts at 169°; the corresponding acid has been described previously (Abstr., 1900, i, 302). When either the acid or the naphthylamine salt is heated above its melting point, *β-naphthylcamphoformeneamine*, $C_8H_{14}<\begin{matrix}C{:}CH{\cdot}NH{\cdot}C_{10}H_7\\ |\\ CO\end{matrix}$, is obtained, which crystallises in slender, pale yellow prisms and melts at 173°. *α-Naphthylamine α-naphthylcamphoformenecarboxylate* melts at 165°.

With *p*-toluidine, the following compounds were obtained. p-*Tolylcamphoformeneaminecarboxylic acid*, $C_8H_{14}<\begin{matrix}C{:}C(NH{\cdot}C_6H_4Me){\cdot}CO_2H\\ |\\ CO\end{matrix}$, crystallises from benzene in pale yellow prisms and melts at 168°; the p-*toluidine* salt melts at 152°. p-*Tolylcamphoformeneamine*, $C_8H_{14}<\begin{matrix}C{:}CH{\cdot}NH{\cdot}C_6H_4Me\\ |\\ CO\end{matrix}$, crystallises from alcohol in slender, yellow prisms and melts at 178°. *m*-Toluidine furnishes m-*tolylcamphoformeneaminecarboxylic acid*, $C_8H_{14}<\begin{matrix}C{:}C(NH{\cdot}C_6H_4Me){\cdot}CO_2H\\ |\\ CO\end{matrix}$, which crystallises from benzene in colourless needles and melts at 154°, and its m-*toluidine* salt melting at 126°; when these compounds are heated above the melting point, a viscous mass is produced in each case from which no definite compound can be isolated. Benzylamine yields *benzylcamphoformeneaminecarboxylic acid*,

$$C_8H_{14}<\begin{matrix}C{:}C(NH{\cdot}C_7H_7){\cdot}CO_2H\\ |\\ CO\end{matrix},$$

which crystallises in colourless prisms and melts at 140°, the *benzylamine* salt melting at 174·5°, and *benzylcamphoformeneamine*,

$$C_8H_{14}<\begin{matrix}C{:}CH{\cdot}NH{\cdot}C_7H_7\\ |\\ CO\end{matrix},$$

which crystallises in colourless prisms and melts at 96·5°.

Diethylamine reacts with camphoroxalic acid with formation of *diethylamine diethylcamphoformolaminecarboxylate*,

$$C_8H_{14}<\begin{matrix}CH\cdot C(OH)(NEt_2)\cdot CO_2H,NHEt_2,\\ |\\ CO\end{matrix}$$

which crystallises from alcohol in colourless needles, melts at 139·5°, and when heated above its melting point is converted into a *compound*, $C_{15}H_{25}ON$, which crystallises in colourless needles and melts at 153°. Dimethylamine similarly yields *dimethylamine dimethylcamphoformolaminecarboxylate*, which crystallises in colourless needles, melts at 137·5°, and when heated above its melting point is decomposed with formation of a *compound*, $C_{13}H_{21}ON$, melting at 63°. *Methylamine methylcamphoformeneaminecarboxylate*,

$$C_8H_{14}<\begin{matrix}C{:}C(NHMe)\cdot CO_2H,NH_2Me,\\ |\\ CO\end{matrix}$$

melts at 172°, and when heated above this temperature is converted into *methylcamphoformeneamine*, $C_8H_{14}<\begin{matrix}C{:}CH\cdot NHMe\\ |\\ CO\end{matrix}$, which crystallises in colourless needles and melts at 131°.

Benzamidine reacts with camphoroxalic acid to form a colourless, crystalline compound, $C_{19}H_{24}O_4N_2$, which melts at 184° and becomes charred at a slightly higher temperature. Benzidine yields a greenish-yellow, crystalline *compound* which melts at 190°. When an alcoholic solution of camphoroxalic acid is heated with 4-nitro-*o*-toluidine under pressure at 150° for several hours, o-*nitrotolylcamphoformeneamine*, $C_8H_{14}<\begin{matrix}C{:}CH\cdot NH\cdot C_6H_3Me\cdot NO_2\\ |\\ CO\end{matrix}$, is produced, which crystallises in bright yellow needles and melts at 192°.

Semicarbazide reacts with camphoroxalic acid with formation of *semicarbazidocamphoformeneaminecarboxylic acid*,

$$C_8H_{14}<\begin{matrix}C{:}C(NH\cdot NH\cdot CO\cdot NH_2)\cdot CO_2H\\ |\\ CO\end{matrix},$$

which crystallises from alcohol in stout, colourless prisms, melting at 200°, and from boiling glacial acetic acid in groups of slender needles, melting at 209—210°; the relationship between these two forms is being investigated.

By the action of benzenesulphonic chloride on phenylcamphoformeneamine, the *phenylsulphone*, $C_8H_{14}<\begin{matrix}C{:}CH\cdot NPh\cdot SO_2Ph\\ |\\ CO\end{matrix}$, is produced, which crystallises in colourless needles and melts at 133°. Acetyl chloride reacts with *p*-tolylcamphoformeneamine with formation of the *acetyl* derivative, $C_8H_{14}<\begin{matrix}C{:}CH\cdot NAc\cdot C_6H_4Me\\ |\\ CO\end{matrix}$, which is a colourless, crystalline compound melting at 161°. When β-naphthylcamphoformeneamine is treated with chloroacetyl chloride, a colourless, crystalline substance is obtained which melts at 63° and is very unstable.

E. G.

New Terpene Alcohol in Myrtle Oil. Hugo von Soden and Fritz Elze (*Chem. Zeit.*, 1905, **29**, 1031).—On subjecting the residues of high boiling point from Spanish myrtle oil to fractional distillation

in a vacuum, the authors obtained a large fraction having a sp. gr. 0·975 at 15° and a_D +28° in a 100 mm. tube, which consisted, to the extent of about 80 per cent., of an ester $CH_3 \cdot CO_2 \cdot C_{10}H_{17}$. This fraction, on hydrolysis with alcoholic potash, yielded an alcohol *myrtenol*, which was purified by conversion into *myrtenyl phthalate*, which separates from light petroleum (b. p. 100—125°) in hard, white crystals melting at 116°; the latter, on hydrolysis, yields pure *myrtenol*, which is a thick, colourless oil of a peculiar odour resembling myrtles; it boils at 220—221° under 751 mm. or at 79·5—80° under 3·5 mm. pressure, has a sp. gr. 0·985 at 15° and a_D +49°25′ in a 100 mm. tube. *Myrtenol* appears to be a cyclic primary alcohol containing a single double linking. P. H.

Constitution of the Group, N_2O_2, of Pernitroso-compounds derived from Oximes. Ottorino Angelucci (*Annalen*, 1905, **341**, 172—182).—The constitution of the group, N_2O_2, of the pernitroso-compounds is best represented by the expression R:N·O·N:O. The peculiar behaviour of the pernitroso-compounds from camphoroxime and certain other oximes is due to the nature of the group combined with the nitroso-group, and not to the nitroso-group itself. Scholl's nitroimines (this vol., i, 181) are considered to be nitroso-compounds.

When pernitrosocamphor is reduced with aluminium amalgam, a mixture of the two stereoisomeric bornylamines is formed. If nitrosyl chloride (1 mol.) and camphoroxime (2 mols.) react in chloroform solution, molecular proportions of pernitrosocamphor and the hydrochloride of camphoroxime are formed. Nitrosyl chloride and sodium camphoroxime react quantitatively to form pernitrosocamphor. K. J. P. O.

Synthetical and Natural Phellandrene. Iwan Kondakoff and Iwan Schindelmeiser (*J. pr. Chem.*, 1905, [ii], **72**, 193—196. Compare Abstr., 1903, i, 845).—*tert.*-Carvomenthyl chloride, obtained from *tert.*-carvomenthol, boils at 83·5—84·5° under 12 mm. pressure, has a sp. gr. 0·932 at 20°/4°, and forms *tert.*-carvomenthene, which boils at 174—176°, has a sp. gr. 0·811 at 20°/4°, and n_D 1·45709. On treatment with bromine in strongly cooled light petroleum solution, this yields carvomenthene dibromide, which boils between 130° and 144° under 11 mm. pressure, has a sp. gr. 1·208 at 20°/4°, is optically inactive, and by alcoholic potassium hydroxide is converted into a hydrocarbon or mixture of hydrocarbons which must have the constitution

$$CH_2{:}CH{<}{\genfrac{}{}{0pt}{}{CH_2 \cdot CH_2}{CH_2 \cdot CH_2}}{>}CHPr^{\beta}.$$

This distils in two fractions: the larger boils at 175—180°, has a sp. gr. 0·825 at 20°/4°, and n_D 1·46693; the smaller boils at 180—185°, has a sp. gr. 0·828 at 20°/4°, and n_D 1·4673. The hydrocarbon is not identical therefore with natural phellandrene. Both fractions are optically inactive and give a red coloration with sulphuric acid in acetic acid solution. A specimen of phellandrene from *Phellandrum aquaticum*, which boils at 165—168°, has a sp. gr. 0·844 at 20°/4°, n_D 1·47575, and $[a]_D$ +8°37′ at 20°, reacts with hydrochloric acid in acetic acid solution to form a dextrorotatory chloro-derivative, $C_{10}H_{17}Cl$,

which melts at 110° and boils at 86° under 11 mm. pressure, and a dichloride, $C_{10}H_{18}Cl_2$, which boils at 122·5—125° under 16 mm. pressure, and has a sp. gr. 1·006 at 20°/4° and n_D 1·48516 at 20° (compare Pesci, Abstr., 1886, 1038). G. Y.

Constitution of Terpinene. T. Amenomiya (*Ber.*, 1905, **38**, 2730—2732. Compare this vol., i, 603).—When terpinene nitronitrosite, formed by the nitration of terpinene nitrosite, is reduced in alcoholic solution with zinc dust and the product then submitted to distillation in a current of steam, rhombic prisms of carvenoneoxime, melting at 91—92°, are obtained. When terpinene nitrosite itself is reduced in a similar manner, carvenone is formed in small amount.

The bearing of these results on the constitution of terpinene is discussed. A. McK.

Oil derived from Leaves and Stems of the Sweet Orange (Citrus Aurantium). Gustave Litterer (*Bull. Soc. chim.*, 1905, [iii], **33**, 1079—1081).—The oil is of a bright yellow colour, has a sp. gr. 0·8603 at 15°, n_D 1·472 at 20°, and a_D +56°46′ in a 100 mm. tube. The principal constituents of the oil are *d*-camphene, limonene, geraniol, *d*-linalool (?), and citral (4 per cent.). The alcohols are present partly in the free state and partly as esters. T. A. H.

Oil derived from the Leaves and Stems of the Lemon Tree (Citrus Limonum). Gustave Litterer (*Bull. Soc. chim.*, 1905, [iii], **33**, 1081—1083).—The oil is yellow in colour, and is of a pleasant odour, has a sp. gr. 0·8824 at 15°, n_D 1·4725 at 23°, and a_D +21°8′ in a 100 mm. tube. It contains the same constituents as the oil obtained from the leaves and stems of the sweet orange (see preceding abstract), but contains more citral (24 per cent.) and esters and less camphene. The "total alcohol" is practically the same for both oils. T. A. H.

Essential Oil of Patchouli. Action of Sulphuric Acid on Oil of Patchouli. Anne W. K. de Jong (*Rec. Trav. chim.*, 1905, [ii], **24**, 309—310, 311—312).—The physical constants of the essences obtained from three varieties of patchouli are as follows: that from flowering patchouli has a sp. gr. 0·922 at 25°, $[a]_D$ −16°10′ at 25°, 10 c.c. dissolve in 100 c.c. alcohol, it begins to distil at 130°, and 50 per cent. distils between 250° and 270°. That from Singapore patchouli has a sp. gr. 0·949 at 25°, $[a]_D$ −51°24′ at 25°, 10 c.c. dissolve in 60 c.c. alcohol, it begins to distil at 230°, 60 per cent. passing over between 250° and 270°. That from Java patchouli has a sp. gr. 0·929 at 25°, $[a]_D$ −42°18′ at 25°, 10 c.c. dissolve in 7·5 c.c. of alcohol; it begins to distil at 145°, and 70 per cent. passes over between 250° and 270°.

By the action of concentrated sulphuric acid on essence of patchouli, a sesquiterpene, $C_{15}H_{24}$, boiling at 260—263° under 740 mm. pressure, is obtained; the hydrocarbon derived from Singapore patchouli has a sp. gr. 0·915 at 25° and $[a]_D$ −1°, whilst that obtained from Java patchouli has a sp. gr. 0·897 at 25° and $[a]_D$ −1°5′ at 25°. The author proposes the name *dilemene* (from *dilem*, the Malay name of the plant)

for this sesquiterpene, which is probably identical with the compound obtained by Soden and Rojahn by fractional distillation of patchouli oil (compare Abstr., 1904, i, 904). M. A. W.

Scammony Resins. P. Guigues (*J. Pharm. Chim.*, 1905, [vi], **22**, 241—246).—Genuine scammony resin of pharmacy contains 20 per cent. of resin insoluble in ether, the rest being soluble; the insoluble resin has a_D $-20°43'$ and n_D 1·3659 at 15°; the corresponding values for the soluble resin are $-21°43'$ and 1·3659 respectively. M. A. W.

The Nature of the Sugars of certain Glucosides. Henri Ter Meulen (*Rec. Trav. chim.*, 1905, [ii], **24**, 444—483).—It has been shown by Croft Hill that the hydrolysis of maltose by maltase is a reversible reaction (compare Trans., 1898, **73**, 634; 1903, **83**, 578), and by Tammann that the hydrolysis of amygdalin by emulsin is retarded by the addition of dextrose to the solution (compare Abstr., 1889, 566; 1892, 899). In the present paper, the author shows that the hydrolytic action of any enzyme on its specific glucoside is retarded by the addition to the solution of the sugar that forms one of the products of the reaction; and, further, the nature of the sugar formed by the hydrolysis of a glucoside can in this way be determined. The experiments were conducted as follows: equal volumes of the glucoside solution were taken and to each was added a definite quantity of a sugar (galactose, lævulose, sucrose, maltose, rhamninose, or dextrose) and of the specific enzyme; after about two hours, the enzyme was destroyed and the extent to which the glucoside had suffered hydrolysis was measured by separating and weighing the product, other than sugar, of the reaction; thus, in the case of xanthorhamnin (compare Votoček and Frič, Abstr., 1901, i, 161; Tanret, Abstr., 1900, i, 78, 185), the glucoside was hydrolysed to the extent of 55—56 per cent. either in solution alone or in solutions containing dextrose, lævulose, galactose, rhamnose, sucrose, lactose, maltose, or raffinose, whilst in a solution containing rhamninose, which is the sugar formed during the hydrolysis, only 39 per cent. of the glucoside was decomposed. Similar experiments conducted on salicin, amygdalin, æsculin, arbutin, coniferin, indican, saponin, and on certain glucosides which could not be obtained in a pure state, such as gluconasturtein, glucotropeolin, glucocochlearin, and gluconapin, showed that in each of these cases dextrose is the sugar formed by the hydrolysis of the glucoside.

The presence in solution of a specific sugar only retards the hydrolysis of the glucoside in the initial stages of the reaction; towards the end of the reaction, the hydrolysis is more complete in the liquid containing the sugar than in the liquid to which no sugar has been added; this is because the enzyme is less rapidly destroyed in a solution containing sugar than in an aqueous solution. M. A. W.

Gentiamarin. Georges Tanret (*Bull. Soc. chim.*, 1905, [iii], **33**, 1071—1073. Compare this vol., i, 655).—The alcoholic extract of gentian root, from which gentiopicrin separates (*loc. cit.*), contains in addition the amorphous glucoside *gentiamarin*, which may be obtained

by washing the extract with ether, dissolving the insoluble matter in water, and adding to this solution (1) a large excess of tannic acid and (2) a solution of magnesium sulphate in water. In this way a "tannate" of the glucoside is precipitated from which the latter may be regenerated by adding hydrated lead oxide to an alcoholic solution of the "tannate." Gentiamarin is bitter, miscible with water or alcohol, has $[\alpha]_D$ -80—$90°$, and the composition $C_{16}H_{22}O_{10}$ or $C_{16}H_{20}O_{10}$. On hydrolysis with acids, it yields dextrose and an amorphous, brown, insoluble substance. Emulsin hydrolyses it with the formation of dextrose and an amorphous, maroon-coloured substance not identical with gentiogenin. T. A. H.

Caryophyllin. JOHANNES HERZOG (*Chem. Centr.*, 1905, ii, 553—554; from *Ber. Deut. pharm. Ges.*, **15**, 121—124. Compare Meyer and Hönigschmid, this vol., i, 456).—Caryophyllin and diphenylcarbamic chloride interact in pyridine solution to form *caryophyllin diphenylcarbamate*, $C_{40}H_{63}O_4{\cdot}CO{\cdot}NPh_2$, which crystallises in needles, melts at 137—138°, and when hydrolysed yields caryophyllin and diphenylamine. When heated with acetic anhydride and sodium acetate, caryophyllin forms a *diacetyl* derivative, $C_{40}H_{62}O_4Ac_2$, which becomes brown at 210° and is completely melted at 255°. The composition of these derivatives is in agreement with caryophyllin, having the formula $C_{40}H_{64}O_4$, which requires $C = 78{\cdot}9$ per cent., but caryophyllin, when dissolved in cold alcohol, leaves a brown, insoluble residue, and the product from the solution, as also caryophyllin which has been purified by sublimation, contains $C = 75{\cdot}7$ per cent. The *potassium* and *barium* salts are described. The crystalline *benzoyl* derivative formed by heating caryophyllin and benzoic anhydride at 200° sinters at 173° and is melted at 185°. The *product* obtained on oxidation of caryophyllin with chromic acid in acetic acid solution at 80° is insoluble in aqueous sodium hydroxide, but dissolves in water, and forms an *oxime* and a *semicarbazone*. G. Y.

Curcumin. C. LORING JACKSON and LATHAM CLARKE (*Ber.*, 1905, **38**, 2712—2713. Compare Jackson and Menke, Abstr., 1882, 1107).—Results of molecular weight determinations and of analyses are given which are in agreement with the formula, $C_{14}H_{14}O_4$, previously ascribed (*loc. cit.*) to curcumin. Ciamician and Silber's formula, $C_{21}H_{20}O_6$ (Abstr., 1897, i, 229), was founded on the results of methoxyl determinations, which must be due to abnormal behaviour of curcumin with hydriodic acid. G. Y.

Rosocyanin. C. LORING JACKSON and LATHAM CLARKE (*Ber.*, 1905, **38**, 2711—2712. Compare Schlumberger, *Bull. Soc. chim.*, 1866, [ii], **5**, 194; Gajewsky, this Journal, 1873, 504, 760).—Rosocyanin, $C_{14}H_{14}O_4$, prepared by heating a mixture of curcumin, boric and sulphuric acids, alcohol, and water on the water-bath, is precipitated, on addition of ether to its rose-coloured, alcoholic solution, as a purplish-red substance, resembling powdered rosaniline, but with a slightly more yellow sheen. The *ammonium*, $C_{14}H_{13}O_4NH_4$, and the *potassium*, $C_{14}H_{13}O_4K$, salts are intensely blue. G. Y.

Preparation of Crystalline Gentiogenin. HENRI HÉRISSEY (*J. Pharm. Chim.*, 1905, [vi], 22, 249—251).—A claim for priority against Tanret (compare Hérissey and Bourquelot, Abstr., 1900, i, 511; 1901, i, 258; ii, 34; and Tanret, this vol., i, 655). M. A. W.

The Carbonyl Group as Tannophore. MAXIMILIAN NIERENSTEIN (*Chem. Centr.*, 1905, ii, 659; from *Collegium*, 1905, 221—222. Compare Baeyer, this Journal, 1873, 501; Caro, Abstr., 1893, i, 274; Kahl, Abstr., 1898, i, 258).—The action of formaldehyde on gallic acid leads to the formation of hexahydroxydiphenylmethanedicarboxylic acid and Caro's hexahydroxyaurincarboxylic acid (*loc. cit.*), which is soluble in water and precipitates gelatin from its aqueous solution. Similarly from formaldehyde and pyrogallol there are obtained hexahydroxydiphenylmethane and a substance which is soluble in water and precipitates gelatin; this must have the constitution

$$O<\begin{matrix}C[C_6H_2(OH)_3]_2\\ | \\ C_6H_2(OH)_2\end{matrix}.$$

The author considers that these facts support his view that the carbonyl group is the tannophore in the tannins. G. Y.

Condensation Products from Tannin, Formaldehyde, and Carbamide or Carbamates. ARNOLD VOSWINKEL (D.R.-P., 160273).—On addition of formaldehyde to an aqueous solution of tannin and carbamide in molecular proportions, a precipitate of *methylenetannincarbamide* is produced;

$$C_{14}H_{10}O_9 + CO(NH_2)_2 + CH_2O = C_{14}H_9O_9 \cdot CH_2 \cdot NH \cdot CO \cdot NH_2 + H_2O.$$

The product is a yellow powder, becoming brown at 220° and then decomposing; it is insoluble in organic solvents with the exception of alcohol, and does not give the biuret reaction.

Carbamates react in similar manner. Thus tannin, ethyl carbamate, and formaldehyde yield the *compound* $C_{14}H_9O_9 \cdot CH_2 \cdot NH \cdot CO_2Et$, which becomes brown and decomposes at 190°, and dissolves in alcohol and alkaline solutions. C. H. D.

Tannins producing a "Bloom" [on Leather]. II. MAXIMILIAN NIERENSTEIN (*Chem. Centr.*, 1905, ii, 527; from *Collegium*, 1905, 197—200. Compare this vol., i, 365).—Algarobilla (*Cæsalpinia brevifolia*) and divi-divi (*C. coriaria*) contain about 40—45 per cent. of pyrogallol tannins, which produce a light-coloured leather that appears blue in section; the blue colour is most probably caused by methyl gallate, which with excess of milk of lime gives a deep blue colour that remains permanent in the leather where it is not exposed, but disappears on exposure to air, forming a colourless, calcium salt. One hundred and forty-five grams of algarobilla husks were extracted with 4 litres of water; after three days, 20 grams of crude ellagic acid separated. The alcoholic mother liquors contained a substance which, on fusion with potassium hydroxide at 185°, yielded phloroglucinol and gallic acid. Tetra-acetylellagic acid melts at 311—313°, and not at 276—279° as previously stated. The aqueous filtrate from the ellagic acid contained *methyl gallate*, $C_8H_8O_5$, which separates from water in small crystals and melts at 189—190°; it gives a blue coloration with

ferric chloride, and also with lime-water, as above described; the aqueous filtrate yielded tannin glucoside, a glassy substance melting at 217—221° (compare A. G. Perkin, Trans., 1897, **71** 1135), which gives an acetyl derivative melting at 127°. P. H.

γ-Hydroxypyrone and some of its Derivatives. I. Non-nitrogenous Derivatives. ALBERTO PERATONER (*Chem. Centr.*, 1905, ii, 678; from *Giorn. Sci. Nat. Econ.*, **25**, 239—244. Compare Peratoner and Leonardi, Abstr., 1900, i, 550).—A theoretical introduction to the following five communications. G. Y.

Constitution of Comenic Acid. ALBERTO PERATONER and F. CARLO PALAZZO (*Chem. Centr.*, 1905, ii, 678; from *Giorn. Sci. Nat. Econ.*, **25**, 245—251).—Ostwald has shown that the introduction of a hydroxyl group in the ortho- or meta-position raises, but in the para-position depresses, the dissociation constant. Comanic acid (pyrone-2-carboxylic acid: Haitinger and Lieben, Abstr., 1885, 965) has the dissociation constant $K = 2{\cdot}8$, whilst comenic acid has $K = 2{\cdot}0$, and is therefore 3-hydroxy-γ-pyrone-6-carboxylic acid. This conclusion is in agreement with the properties of comanamic and comenamic acids, which are weak acids and have the dissociation constants $K = 0{\cdot}0266$ and 0·0241 respectively (compare Ost, Abstr., 1885, 49). G. Y.

Alkyl Ethers of Pyromeconic Acids. ALBERTO PERATONER and ROSARIO SPALLINO (*Chem. Centr.*, 1905, ii, 678—679; from *Giorn. Sci. Nat. Econ.*, **25**, 252—258).—The constitution previously assumed for pyromeconic acid (Peratoner and Leonardi, Abstr., 1900, i, 550) is confirmed by the formation of 3-ethoxy-γ-pyrone (Olivieri-Tortorici, Abstr., 1902, i, 302) by the action of diazoethane on the acid.

The action of diazomethane on pyromeconic acid leads to the formation of *3-methoxy-γ-pyrone*, $CH{<}{\begin{matrix}O-CH\\CH\cdot CO\end{matrix}}{>}C\cdot OMe$, which crystallises from a mixture of petroleum and benzene, sublimes in a vacuum at 100—110° in hard, colourless scales, melts at 85°, and when hydrolysed with calcium oxide yields formic acid and acetylcarbinol methyl ether (Leonardi and de Franchis, Abstr., 1903, i, 787).

This reaction forms a general method for the determination of the constitution of simple hydroxy-derivatives of γ-pyrone, as on methylation with diazomethane and subsequent hydrolysis, those derivatives which have one or two hydroxyl groups in neighbouring positions to the carbonyl must yield acetylcarbinol methyl ether or the methyl ether of dihydroxyacetone, which are identified best as the *p*-nitrophenylhydrazones. G. Y.

Constitution of Hydroxycomenic Acid (Dihydroxypyronecarboxylic Acid). ALBERTO PERATONER and V. CASTELLANA (*Chem. Centr.*, 1905, ii, 679—680; from *Giorn. Sci. Nat. Econ.*, **25**, 259—271. Compare Tickle and Collie, Trans., 1902, **81**, 1004).—Bromocomenic acid is prepared best by adding 1 mol. of bromine in acetic acid solution to 1 mol. of meconic acid dissolved in acetic acid and

evaporating the mixture under reduced pressure, or by subjecting powdered meconic acid to the action of bromine vapour for 36—48 hours. When boiled with dilute hydrochloric acid in a reflux apparatus, it is converted into hydroxycomenic acid, which, when acted on by hydrogen chloride in methyl-alcoholic solution at the laboratory temperature, forms *methyl hydroxycomenate*,

$$C_5HO_2(OH)_2\cdot CO_2Me.$$

This crystallises in slender, white needles, melts at 222°, is easily hydrolysed by boiling water, and gives a red coloration with traces, or a blue coloration with excess, of ferric chloride. *Methyl dimethoxy-γ-pyronecarboxylate*, $C_5HO_2(OMe)_2\cdot CO_2Me$, formed by the action of diazomethane on the methyl dihydroxy-ester in ethereal solution, crystallises in long, colourless needles, melts at 97°, and when boiled with very dilute hydrochloric acid yields *dimethoxy-γ-pyronecarboxylic acid*, $C_5HO_2(OMe)_2\cdot CO_2H$, which crystallises in glistening scales and melts at 242°. When hydrolysed with baryta, the methyl dimethoxy-ester yields 1 mol. each of acetylcarbinol methyl ether, carbon dioxide, and oxalic acid, and 2 mols. of methyl alcohol; the methoxy-groups are therefore in the positions 2 and 3, and the constitution

$$OH\cdot C{<}{C(OH)\cdot O \atop CO-CH}{>}C\cdot CO_2H$$

for hydroxycomenic acid is confirmed. G. Y.

Constitution of Maltol. ALBERTO PERATONER and ANTONIO TAMBURELLO (*Chem. Centr.*, 1905, ii, 680; from *Giorn. Sci. Nat. Econ.*, **25**, 272—289. Compare Abstr., 1904, i, 61).—Maltol reacts with phenylcarbimide to form the *phenylcarbamate*, $C_5H_2O_2Me\cdot O\cdot CO\cdot NHPh$, which crystallises in rosettes of hard needles, melts at 149—150°, and sublimes. The *methyl ether* of maltol, $C_5H_2O_2Me\cdot OMe$, formed by adding powdered dry maltol to an ethereal solution of diazomethane, is a colourless oil which boils at 114° under 15 mm. pressure, and in presence of even traces of impurities rapidly becomes red. When hydrolysed with baryta, it yields 1 mol. each of acetylcarbinol methyl ether and formic and acetic acids. Methyl alcohol is detected amongst the hydrolysis products by shaking the solution with freshly precipitated platinum black and adding phloroglucinol and potassium hydroxide solutions to the filtrate, when the characteristic red colour is obtained. The methyl ether has therefore the constitution

$$CH{<}{O-CMe \atop CH\cdot CO}{>}C\cdot OMe \text{ or } CMe{<}{O-CH \atop CH\cdot CO}{>}C\cdot OMe,$$

of which only the former can correspond to maltol, as this does not react with amyl nitrite or with diazonium acetate, sulphuryl chloride, and iodic acid (compare Peratoner, Abstr., 1902, i, 421), showing that it has the constitution which does not allow of change into the ketonic modification. G. Y.

Pyridones from Pyromeconic Acid and Maltol. ALBERTO PERATONER and ANTONIO TAMBURELLO (*Chem. Centr.*, 1905, ii, 680—681; from *Giorn. Sci. Nat. Econ.*, **25**, 290—297).—When heated with dilute ammonia and evaporated to dryness on the water-bath,

the alkyl ethers of pyromeconic acid and maltol are converted into the corresponding alkoxypyridones.

3-*Methoxy*-4-*pyridone*, $C_6H_7O_2N,3H_2O$, prepared from methyl pyromeconate, crystallises in small, glistening needles, melts at 114°, loses $3H_2O$ on prolonged heating at 100°, melts when anhydrous at 173°, sublimes in a vacuum at about 200°, gives an intense yellow coloration with ferric chloride, and when boiled with hydriodic acid yields 3-hydroxy-4-pyridone (pyrocomenamic acid: Ost, Abstr., 1883, 792).

3-*Ethoxy*-4-*pyridone*, $C_7H_9O_2N,H_2O$, crystallises in rosettes of glistening plates, melts when quickly heated at 112—113°, or after prolonged heating at 100°, or drying over sulphuric acid in a vacuum at 135—136°, sublimes in a vacuum, gives a yellow coloration with ferric chloride, and by boiling hydriodic acid is converted into 3-hydroxy-4-pyridone.

3-*Methoxy*-2-*methyl*-4-*pyridone*, $C_7H_9O_2N$, formed from maltol, crystallises in small, hard, glistening needles, melts at 149°, sublimes in a vacuum at 220°, gives an intense yellow coloration with ferric chloride, and is converted by boiling hydriodic acid into 3:4-*dihydroxy*-2-*methylpyridine hydriodide*, which crystallises in white, glistening leaflets. The free *base*, $C_6H_7O_2N$, crystallises in small, hard, glistening needles, decomposes at about 250°, sublimes in a vacuum, and gives with ferric chloride a red coloration, which on addition of more ferric chloride becomes violet and finally blue. The *acetyl* derivative, $C_6H_6O_2NAc$, crystallises in hard, glistening needles, melts at 204—205°, and sublimes.

The *acetyl* derivative of 3-hydroxy-4-pyridone, $C_7H_7O_3N$, crystallises in hard needles and melts at 207—208°. G. Y.

An Isomeride of Kaempferol. STANISLAUS VON KOSTANECKI and B. SCHREIBER (*Ber.*, 1905, **38**, 2748—2751. Compare Abstr., 1904, i, 607, 683).—2′-*Hydroxy*-3′:4′:4-*trimethoxychalkone*,

$$OH\cdot C_6H_2(OMe)_2\cdot CO\cdot CH:CH\cdot C_6H_4\cdot OMe,$$

prepared by the condensation of gallacetophenone dimethyl ether with anisaldehyde, separates from alcohol in yellow plates and melts at 131—132°. The *acetyl* derivative forms pale yellow needles and melts at 89—90°.

7:8:4′-*Trimethoxyflavanone*, $C_{18}H_{18}O_5$, forms white needles and melts at 115°. Its iso*nitroso*-derivative separates from benzene in pale yellow leaflets and melts and decomposes at 152°. It yields a brownish-yellow shade with cobalt mordants.

7:8:4′-*Trimethoxyflavonol*, $C_{18}H_{18}O_6$, forms pale yellow needles and melts at 198°. It forms a yellow sodium salt and produces a pale yellow shade with aluminium mordants. Its *acetyl* derivative separates from dilute alcohol in needles and melts at 157°.

7:8:4′-*Trihydroxyflavonol*, $C_6H_2(OH)_2<\begin{matrix}O—C\cdot C_6H_4\cdot OH \\ CO\cdot C\cdot OH\end{matrix}$, prepared from the trimethoxyflavonol by boiling with concentrated hydriodic acid, separates from alcohol in yellow needles and melts and decomposes at 319°. It dissolves in sodium hydroxide to an orange solution. It yields orange shades with aluminium mordants. Its

acetyl derivative separates from dilute alcohol in needles and melts at 175°. A. McK.

Condensation of Hydroxyquinol with Aldehydes. ERWIN HEINTSCHEL (*Ber.*, 1905, **38**, 2878—2883. Compare Liebermann and Lindenbaum, Abstr., 1904, i, 443, 764).—The following fluorones, which melt above 300°, were obtained in the form of their sulphates by adding 15 per cent. sulphuric acid to an alcoholic solution of hydroxyquinol and the aldehyde.

2 : 3 : 7-*Trihydroxy*-9-m-*nitrophenylfluorone*,

$$\left.\begin{array}{l} OH{\cdot}C{:}CH{\cdot}C{:}C(C_6H_4{\cdot}NO_2) \\ O{:}C{\cdot}CH{:}C\text{———————}O \end{array}\right>C_6H_2(OH)_2,$$

from *m*-nitrobenzaldehyde and hydroxyquinol, crystallises in small, metallic, reddish-brown prisms, is sparingly soluble in glacial acetic acid, alcohol, or acetone, forming solutions with yellowish-green fluorescence, and dissolves in aqueous alkali hydroxides to form bluish-red solutions. The *sulphate*, $C_{19}H_{11}O_7N,H_2SO_4,H_2O$, forms brown, metallic needles and yields the free dye on addition of boiling water to its solution in alcohol containing a few drops of sulphuric acid. The *acetyl* derivative, $C_{25}H_{17}O_{10}N$, crystallises in orange needles and melts at 184°.

2 : 3 : 7-*Trihydroxy*-9-m-*bromophenylfluorone*, $C_{19}H_{11}O_5Br$, from *m*-bromobenzaldehyde and hydroxyquinol, forms glistening, scarlet prisms. The *sulphate*, $C_{19}H_{11}O_5Br,H_2SO_4,3H_2O$, forms brown, metallic needles and loses $3H_2O$ at 110°. The *acetyl* derivative, $C_{25}H_{17}O_8Br$, crystallises in brown needles and melts at 242°.

p-*Phenylenebis*-2 : 3 : 7-*trihydroxyfluorone*,

$$C_6H_4\left[C{<}\begin{array}{l} C_6H_2(OH)_2\text{-} \\ C_6H_2O(OH) \end{array}{>}O\right]_2,$$

formed from terephthalaldehyde and hydroxyquinol, crystallises in dark brown, microscopic needles and is sparingly soluble in boiling nitrobenzene. The *sulphate*, $3C_{32}H_{18}O_{10},2H_2SO_4,9H_2O$, forms dark brown, microscopic needles and yields the free dye on repeated boiling with alcohol and water. The *acetyl* derivative, $C_{44}H_{30}O_{16}$, forms a brown, crystalline powder and melts above 300°.

2 : 3 : 7-*Trihydroxy*-9-5′-*nitro*-2′-*hydroxyphenylfluorone*, $C_{19}H_{11}O_8N$, crystallises in glistening prisms or cubes. The *sulphate*,

$$C_{19}H_{11}O_8N,H_2SO_4,2H_2O,$$

forms brown, microscopic needles; the *acetyl* derivative, $C_{27}H_{19}O_{12}N$, crystallises in orange-red needles and melts at 193°.

The fluorone *sulphate* obtained from 5-bromosalicylaldehyde forms red prisms mixed with a small quantity of colourless leaflets; the free *base* contains less bromine than is required for the formula $C_{19}H_{11}O_6Br$. When boiled with zinc dust, sodium acetate, and acetic anhydride, it yields 2 : 3 : 6 : 7-*tetra-acetoxy*-9-o-*acetoxyphenylxanthen*, $C_{29}H_{24}O_4$, which is obtained also by simultaneous reduction and acetylation of 2 : 3 : 7-trihydroxy-9-*o*-hydroxyphenylfluorone. It forms a white, crystalline powder, and melts at 196°. The colourless leaflets obtained along with the sulphate are soluble in ether, and, on acetylation, yield 7-*bromo*-2 : 3-*diacetoxyxanthen*, $C_{17}H_{13}O_5Br$, which

forms feathery aggregates of colourless crystals, melts at 146°, and is moderately soluble in alcohol, acetone, glacial acetic acid, or benzene.

The *sulphate* obtained from 3 : 5-dibromosalicylaldehyde and hydroxyquinol crystallises in dichroic, bluish-red prisms and yields the *fluorone*, $C_{19}H_{11}O_6Br$. This, when boiled with zinc dust, sodium acetate, and acetic anhydride, forms 2 : 3′: 6 : 7-*tetra-acetoxy*-9-2′-*acetoxy*-3′-*bromophenylxanthen*, $C_{29}H_{23}O_{11}Br$, which melts at 210°. Along with the sulphate, there is formed a substance which crystallises in colourless leaflets, and on acetylation yields a *product*, $C_{17}H_{13}O_5Br$, melting at 242—243°. On prolonged simultaneous reduction and acetylation, this yields a halogen-free *product* which melts at 184°, and is not identical with Liebermann and Lindenbaum's diacetoxyxanthen.

When boiled for 10—12 hours with zinc dust, sodium acetate, and acetic anhydride, 5-bromosalicylaldehyde yields *o*-acetoxybenzaldehyde diacetate, melting at 101°. 3 : 5-Dibromosalicylaldehyde, when boiled for 8 hours with zinc dust, sodium acetate, and acetic anhydride, yields 3-*bromo*-2-*acetoxybenzaldehyde diacetate*, $C_{13}H_{13}O_6Br$, which crystallises in prisms and melts at 134°. G. Y.

Action of Carbon Disulphide and Potassium Hydroxide on Ketones. II. HERMANN APITZSCH (*Ber.*, 1905, 38, 2888—2899. Compare Abstr., 1904, i, 510).—The results of analyses are quoted, showing that the orange compound previously described as 1-keto-2 : 6-diphenyl-4-thiophen-3 : 5-dithiol is 4-keto-3 : 5-diphenylpenthiophen-2 : 6-dithiol, $S<\begin{matrix}C(SH){:}CPh\\C(SH){:}CPh\end{matrix}>CO$, yielding the compound

$$S<\begin{matrix}CH_2{\cdot}CHPh\\CH_2{\cdot}CHPh\end{matrix}>CO$$

on reduction, and that the formulæ for the derivatives of the orange compound must be altered accordingly.

The following derivatives of penthiophen are formed in the same manner.

4-*Keto*-3 : 5-*dimethylpenthiophen*-2 : 6-*dithiol*, $C_7H_8OS_3$, formed from diethyl ketone, crystallises in long, orange prisms, melts and decomposes at 157°, and is easily soluble in ethyl acetate, hot alcohol, toluene, xylene, or ethylene dibromide, but only sparingly so in ether, benzene, chloroform, or cold alcohol. The *sodium* derivative, $C_7H_6OS_3Na_2$, forms yellow crystals, and in aqueous solution forms coloured precipitates with the salts of the heavy metals. The *dimethyl* ether, $C_9H_{12}OS_3$, forms long, colourless needles and melts at 123°; the *diethyl* ether forms straw-coloured prisms and melts at 70°; the *dibenzyl* ether, $C_{21}H_{20}OS_3$, crystallises in colourless, glistening needles and melts at 65·5—66°. The *diacetyl* ester, $C_{11}H_{12}O_3S_3$, crystallises in small, yellow needles, becomes red at 100°, and melts and decomposes at about 109—112°; the *dibenzoyl* ester, $C_{21}H_{16}O_3S_3$, crystallises from light petroleum and melts at 105°.

4-*Keto*-3-*methylpenthiophen*-2 : 6-*dithiol*, $C_6H_6OS_3$, formed from methyl ethyl ketone, crystallises in small, orange needles, and melts at 144·5—145°. The *sodium* derivative, $C_6H_4OS_3Na_2,2C_2H_6O$, crystallises from alcohol in yellow nodules and forms coloured precipitates with

salts of the heavy metals in aqueous solution. The *dimethyl ether*, $C_8H_{10}OS_3$, crystallises in yellow needles and melts at 89·5°. The *diacetyl* ester, $C_{10}H_{10}O_3S_3$, forms red needles and melts at 85·5—86°.

4-*Keto*-3 : 5-*diethylpenthiophen*-2 : 6-*dithiol*, $C_9H_{12}OS_3$, formed in small yield from dipropyl ketone, crystallises from chloroform and light petroleum in orange needles and melts at 118°.

4-*Keto-3-phenylpenthiophen*-2 : 6-*dithiol*, $C_{11}H_8OS_3$, formed from benzyl methyl ketone, crystallises in slender needles and melts at 135°.

4-*Keto-3-phenyl-5-methylpenthiophen*-2 : 6-*dithiol*, $C_{12}H_{10}OS_3$, formed from benzyl ethyl ketone, separates from acetone and light petroleum in red crystals and melts at 146°.

The action of carbon disulphide and potassium hydroxide on acetone leads to the formation of a red, amorphous *product* which could not be purified. G. Y.

Quinine Salts and Ammonium Salts. P. Guigues (*J. Pharm. Chim.*, 1905, [vi], 22, 303—306).—In an earlier paper (compare *Bull. trav. Soc. Pharm., Bordeaux*, December, 1900), the author pointed out that the crystallisation of quinine arsenate is accelerated by the addition of ammonium arsenate to the solution, and in the present paper he shows that the reaction is a general one, for if to a solution of quinine sulphate containing a little free sulphuric acid a solution of an ammonium salt (acetate, arsenate, arsenite, borate, bromide, carbonate, chloride, citrate, glycerophosphate, lactate, oxalate, phosphate, tartrate, valerate) is added, a mixture of quinine sulphate and the quinine salt of the other acid separates readily in a crystalline form; whereas, if the quinine sulphate is dissolved in acetic, citric, hydrochloric, lactic, phosphoric, tartaric, or valeric acid and the corresponding ammonium salt added, the quinine salt of the acid separates readily in a crystalline form and in a state of purity.

M. A. W.

Derivatives of Meroquinine. I. Paul Rabe and Karl Ritter (*Ber.*, 1905, 38, 2770—2773).—Cinchinonic acid and the *nitrile* of *methylmeroquinine* are obtained from von Miller and Rhode's *iso*nitrosomethylcinchotoxine (Abstr., 1901, i, 95; compare Rabe and Denham, Abstr., 1904, i, 517; Rhode and Schwob, this vol., i, 228) by the Beckmann decomposition.

The nitrile, $CH_2<\begin{smallmatrix}NMe\cdot CH_2\cdot CH_2\\CH(CH{=}CH_2)\end{smallmatrix}>CH\cdot CH_2\cdot CN$, has strongly basic properties and is volatile in steam. It is a colourless oil with an odour of piperidine, and boils at 252—255° under 741 mm. pressure. The *methiodide*, $C_{11}H_{19}N_2I$, decomposes at 264—265°. The *picrate* melts at 93—95° and the *picrolonate*, $C_{20}H_{24}O_5N_6$, is sparingly soluble and crystallises from alcohol in prismatic needles, melting at 194—195° and insoluble in ether. The *aurichloride*, $C_{10}H_{17}N_2AuCl_4$, melts at 121—123°. J. J. S.

Separation of Conium Alkaloids. Julius von Braun (*Ber.*, 1905, 38, 3108—3112. Compare Hofmann, Abstr., 1885, 562; Wolffenstein, *ibid.*, 1894, i, 627; 1895, i, 253).—The mixture of

alkaloids obtained from conium and containing *d*- and *l*-coniines, *d*- and *l*-methylconiines, γ-conicein, conhydrine, and ψ-conhydrine may be separated by the following method. The mixture is distilled and the portion passing over below 190° collected. The residue solidifies and, after crystallisation from ether, consists of pure conhydrine. The distillate is benzoylated, the product dissolved in ether, and any tertiary base removed by shaking with dilute acid. The ethereal solution is evaporated and the residue mixed with light petroleum. Benzoylconiine goes into solution and a considerable portion of the benzoyl-4-aminobutyl propyl ketone (from coniceine, see following abstract) remains undissolved. The light petroleum solution is evaporated and the residue distilled under reduced pressure. Benzoylconiine passes over at 200—210° under 16 mm. pressure, and the rest of the benzoylated ketone is left in the flask. The amounts of products obtained from 104 grams of mixture were: conhydrine 1, tertiary base 7, benzoylaminobutyl propyl ketone 52 (= coniceine 26), and benzoylconiine 124 (= coniine 68 grams).

The tertiary base is a methylconiine. It distils at 176° under 751 mm. pressure, has a sp. gr. 0·7975 and $[\alpha]_D$ +35·66° at 24'. The *picrate* melts at 114°, is sparingly soluble in hot water, but readily in alcohol. The *aurichloride* crystallises in yellow needles and melts at 82—90°. The relationship of these compounds to those described by Wolffenstein (*loc. cit.*) and Ahrens (Abstr., 1902, i, 390) has not been settled. J. J. S.

γ-Coniceine. I. JULIUS VON BRAUN and ADOLF STEINDORFF (*Ber.*, 1905, **38**, 3094—3107. Compare Hofmann, Abstr., 1885, 562; Lellmann, *ibid.*, 1889, 901; 1890, 1328; Wolffenstein, *ibid.*, 1895, i, 253, 479).—When benzoylated by the Schotten-Baumann method, the ring of γ-coniceine is ruptured and *benzoyl-δ-aminobutyl propyl ketone*,

$$COPh\cdot NH\cdot[CH_2]_4\cdot CO\cdot C_3H_7,$$

is formed. It crystallises from warm water in slender needles, or from a mixture of ether and light petroleum in prisms, and dissolves in most organic solvents. It yields a *phenylsemicarbazone*,

$$C_{22}H_{28}O_2N_4,$$

melting at 150° and sparingly soluble in cold alcohol. Other acyl chlorides react similarly to benzoyl chloride. *Anisoylaminobutylpropyl ketone*, $OMe\cdot C_6H_4\cdot CO\cdot NH\cdot[CH_2]_4\cdot CO\cdot C_3H_7$, crystallises from warm ether and melts at 80°. The *semicarbazone*, $C_{17}H_{26}O_3N_4$, melts at 144°; the *oxime* crystallises in colourless plates melting at 123°.

Both the benzoyl and anisoyl derivatives, when hydrolysed with concentrated hydrochloric acid at 120°, yield coniceine and the corresponding acid. Coniceine picrate melts at 72—73°; Wolffenstein gives 62°.

Coniceine, after purification by distillation in steam, does not give the characteristic greenish-red coloration when its solution in hydrochloric acid is evaporated; whereas the base, which has been purified by distillation under atmospheric pressure, gives an intense colour.

The benzoyl derivative condenses with sodium and ethyl acetate or oxalate yielding oily products. With sodium and amyl formate and subsequent addition of acid, an *oil*, $C_{16}H_{19}O_2N$, distilling at

230—235° under 15 mm. pressure is obtained. It is not an oxymethylene compound, as it does not give any coloration with ferric chloride. Its *semicarbazone* melts at 190°, and when heated for several hours with concentrated acids yields benzoic and butyric acids together with tetrahydropyridine. The probable transformations are :

$$COPh{\cdot}NH{\cdot}[CH_2]_4{\cdot}CO{\cdot}C_3H_7 \longrightarrow COPh{\cdot}NH{\cdot}[CH_2]_3{\cdot}C(CH{\cdot}OH){\cdot}CO{\cdot}C_3H_7$$
$$\longrightarrow COPh{\cdot}N{<}{\begin{matrix}CH{:}C(CO{\cdot}C_3H_7)\\ CH_2{-\!\!-\!\!-\!\!-}CH_2\end{matrix}}{>}CH_2 \longrightarrow NH{<}{\begin{matrix}CH{=}CH\\ CH_2{\cdot}CH_2\end{matrix}}{>}CH_2.$$

Coniceine yields an *additive compound* with benzaldehyde in the form of a reddish-yellow oil, soluble in ether, alcohol, or dilute acids. The acid solution is pale yellowish-red, but gradually assumes a green colour. The *platinichloride* of the additive compound decomposes at 155° and the *aurichloride* forms a yellow precipitate which rapidly sets to a resin.

Coniceine and nitrous acid yield nitrogen and a *compound*, $C_8H_{14}O$, boiling at 150°. The behaviour of coniceine towards benzoyl chloride, taken in conjunction with Lipp's experiments on tetrahydropicoline (Abstr., 1896, i, 317) and Wallach's on a similar base (*Annalen*, 1899, **309**, 28; 1901, **319**, 104), indicate that the grouping $>N{\cdot}C{:}C{:}$ in a ring is unstable, the ring showing a great tendency to rupture. J. J. S.

Synthetical Bases from Methylmorphol and Thebaol and their Behaviour towards Reagents which Decompose Methylmorphimethine. LUDWIG KNORR (*Ber.*, 1905, **38**, 3143—3153. Compare Abstr., 1889, 1218).—*Phenyl dimethylaminoethyl ether*, $C_{10}H_{15}ON$, formed when dimethylchloroethylamine and phenol are heated with sodium ethoxide in alcoholic solution at 120°, boils at 232° under 750 mm. pressure, has a slight odour, and is easily soluble in alcohol or ether; the *aurichloride*, $C_{10}H_{15}ON,HAuCl_4$, forms glistening, yellowish-red leaflets and melts at 124—125°.

3-*Methoxy*-4-*dimethylaminoethoxyphenanthrene*,

$$\begin{array}{l}C(O{\cdot}C_2H_4{\cdot}NMe_2){\cdot}C{-\!\!-\!\!-\!\!-\!\!-}C{\cdot}CH{:}CH\\ C(OMe){\cdot}CH{:}CH{\cdot}C{\cdot}CH{:}CH{\cdot}C{\cdot}CH{:}CH\end{array},$$

is formed when dimethylchloroethylamine hydrochloride and methylmorphol are heated with sodium ethoxide in alcoholic solution, in an atmosphere of nitrogen, in a sealed tube at 150—160°. It is obtained as a colourless, viscid oil, which is easily soluble in alcohol and ether; the *hydrochloride*, $C_{19}H_{21}O_2N,HCl$, crystallises in silvery leaflets and melts at 214—215°; the *picrate* crystallises in slender, yellow needles and melts at 189°; the crystalline *methiodide*, $C_{19}H_{21}O_2N,MeI$, melts at 196—198°. The base is not acted on by *N*-alcoholic sodium ethoxide at 150°, but is decomposed by hydrogen chloride, with formation of morphol, tetramethylethylenediamine, and dimethylaminoethyl alcohol, and when treated with acetic anhydride yields dimethylaminoethyl alcohol and acetylmethylmorphol.

3 : 6-*Dimethoxy*-4-*dimethylaminoethoxyphenanthrene*, $C_{20}H_{23}O_3N$, obtained by heating thebaol with dimethylchloroethylamine and sodium ethoxide in alcoholic solution, forms a viscid oil; the *picrate*,

$$C_{20}H_{23}O_3N,C_6H_3O_7N_3,$$

crystallises from boiling alcohol in matted, slender needles and melts at 186°; the *methiodide*, $C_{20}H_{23}O_3N,MeI,1\frac{1}{2}CH_4O$, crystallises in glistening leaflets, loses $1\frac{1}{2}CH_4O$ at 120°, and melts at 199—200°. The base is not acted on by *N*-alcoholic sodium ethoxide at 150°, but when heated with acetic anhydride at 170° yields acetylthebaol and ethanoldimethylamine.

These facts agree with the author's supposition that methylmorphimethine contains the group $-O\cdot C_2H_4\cdot NMe_2$. G. Y.

Degradation of Morphothebaine to Non-nitrogenous Phenanthrene Derivatives. LUDWIG KNORR and ROBERT PSCHORR (*Ber.*, 1905, **38**, 3153—3159. Compare Knorr, Abstr., 1903, i, 849; Pschorr and Massaciu, Abstr., 1904, i, 767).—*Tribenzoylmorphothebaine*, $C_{39}H_{31}O_6N,C_4H_{10}O$, formed by boiling morphothebaine hydrochloride with benzoyl chloride in a reflux apparatus, crystallises from a mixture of chloroform and ether and melts at 120° or, after loss of $C_4H_{10}O$, at 181°.

Dimethylthebainemethine methiodide, $C_{22}H_{28}O_3NI$, is formed by the action of sodium methoxide and methyl iodide on morphothebaine in methyl-alcoholic solution at 100°, or of methyl sulphate and sodium hydroxide on morphothebaine methiodide in aqueous solution at 100°. It forms shimmering leaflets, decomposes and melts at 266—268°, and when boiled with aqueous sodium hydroxide yields trimethylamine, trimethoxyvinylphenanthrene, and a grey, sandy *powder*, $(C_{19}H_{18}O_3)_x$, which sinters at 200—300° and is sparingly soluble in most solvents. *Trimethoxyvinylphenanthrene*, $C_{16}H_9(OMe)_3$, obtained in this manner, separates from its alcoholic solution, on addition of water, as an oil which solidifies in prisms. It melts at 60—61°, dissolves in the usual organic solvents to form solutions with slight bluish-violet fluorescence, is not acted on by boiling glacial acetic acid, and is isomeric with the trimethoxyvinylphenanthrene obtained from thebinine, which must have the vinyl group in the ortho- or the meso-position. The *picrate*, $C_{19}H_{18}O_3,C_6H_3O_7N_3$, crystallises in reddish-violet needles and melts at 125—126°. The vinyl compound decolorises a chloroform solution of less than 1 mol. of bromine, and when oxidised with potassium permanganate in aqueous acetone solution yields a *trimethoxyphenanthrenecarboxylic acid*, $C_{18}H_{16}O_5$, which crystallises in slender, yellow needles, melts at 201°, and distils with only slight decomposition under 30 mm. pressure, yielding feathery crystals which melt at 181°; on prolonged boiling in a reflux apparatus, it yields a viscid *oil* which is insoluble in aqueous alkali hydroxides and may be 3 : 4 : 6-trimethoxyphenanthrene.

A table is given showing the melting points of the derivatives obtained from morphothebaine and from thebenine; as both these are formed from thebaine, but yield isomeric derivatives, intramolecular change must take place in the formation or in the decomposition of at least one of the two bases. G. Y.

Esterification of Polyhydric Alcohols by Phosphoric and Phosphorous Acids. PAUL CARRÉ (*Ann. Chim. Phys.*, 1905, [viii], **5**, 345—432).—A memoir giving a detailed account of work for the

most part already published (Abstr., 1902, i, 131, 338; 1903, i, 307, 405, 456, 598; 1904, i, 16, 133, 215, 281, 819, 974. Compare Power and Tutin, Trans., 1905, 87, 249). *Brucine glycylphosphate*, $PO(OH)_2\cdot O\cdot C_2H_5O,(C_{23}H_{26}O_4N_2)_2,12H_2O$, crystallises in small prisms, melts at 181°, and is soluble in warm water, less so in cold, and insoluble in ether. *Brucine hydrogen glycylphosphate* crystallises (with $3H_2O$) in needles, melts at 176°, and is readily soluble in water and alcohol. The neutral and basic quinine salts (Abstr., 1904, i, 282) melt at 169° and 123° respectively.

Brucine glycerolphosphate crystallises in needles with $9H_2O$, becomes anhydrous at 100°, melts at 181°, is soluble in alcohol or warm water, less so in cold water, and insoluble in ether. *Brucine hydrogen glycerolphosphate* crystallises from water in needles and melts at 176°.

Brucine erythritolphosphate crystallises from water in prisms (containing $12H_2O$), melts at 169°, and is very soluble in water or alcohol. The *acid* salt separates from its solution in water, on addition of acetone, in slender, efflorescent needles containing $4H_2O$, becomes anhydrous at 100°, and melts at 166°.

Quinine erythritolphosphate crystallises in slender needles and melts at 138°. *Quinine hydrogen erythritolphosphate* separates in needles which contain water of crystallisation, but the salt is efflorescent and rapidly becomes anhydrous, and then melts at 191°.

When dihydrogen erythritolphosphate (Abstr., 1903, i, 307) is warmed, it is converted into the *di-ester*, $OH\cdot PO<\begin{matrix}O\cdot CH\cdot CH_2 \\ O\cdot CH\cdot CH_2\end{matrix}>O$, which crystallises in small prisms, decomposes at 205°, is mono-acidic, and on solution in water is rapidly converted into the mono-ester.

Brucine mannide phosphate, $PO(OH)_2\cdot O\cdot C_6H_9O_3,(C_{23}H_{26}O_4N_2)_2,10H_2O$, separates from its solutions in water on addition of acetone in clusters of slender needles and melts at 179°. The analogous *quinine* salt contains $2H_2O$, crystallises in needles, and melts at 136°. *Mannide diphenylurethane*, $C_6H_8O_4(CO\cdot NHPh)_2$, crystallises in spangles and melts at 243°

A general *résumé* of the author's results is given in the original.

T. A. H.

*iso*Strychnine. A. Bacovescu and Amé Pictet (*Ber.*, 1905, 38, 2787—2792. Compare Gal and Étard, Abstr., 1879, 387; Tafel, Abstr., 1891, 1262).—*iso*Strychnine, obtained when strychnine is heated with water in a sealed tube at 160—180°, crystallises from hot water in prismatic needles containing $3H_2O$. It melts at 214·5°, is soluble in about 65 parts of hot water, sparingly in benzene or chloroform, and insoluble in ether, light petroleum, or alkalis, and is optically inactive. It gradually becomes brown in contact with acids or alkalis, and is probably identical with Gal and Étard's trihydrostrychnine. The anhydrous base, $C_{21}H_{22}O_2N_2$, crystallises from benzene in glistening needles melting at 214—215°. The *hydrochloride*, $C_{21}H_{22}O_2N_2,HCl,3H_2O$, melts and decomposes at about 314°. The *platinichloride* and *aurichloride* are pale yellow, amorphous precipitates. The *mercurichloride* is crystalline and melts at 228°, and the *picrate*, also crystalline, blackens at about 245°.

*iso*Strychnine gives a purple coloration with potassium dichromate and concentrated sulphuric acid, but this rapidly changes to yellow. With bromine water, it gives a pale yellow precipitate, and with warm ferric chloride solution a red coloration. With Mandelin's reagent, it gives a pale brown coloration, and also readily reduces gold, platinum, and silver salts. When boiled for six hours with sodium ethoxide solution, the base yields Tafel's *iso*strychnic acid.

It is not so strongly toxic as strychnine, and its physiological properties more closely resemble those of brucine than of strychnine.

J. J. S.

Strychnine Oxide. Amé Pictet and Max Mattisson (*Ber.*, 1905, **38**, 2782—2787).—*Strychnine oxide*, $C_{21}H_{22}O_3N_2,3H_2O$, is obtained when strychnine is warmed on the water-bath with 3 per cent. hydrogen peroxide solution. It crystallises in large, colourless, monoclinic prisms [$a : b : c = 2·1280 : 1 : 2·5300$] and has the properties of an aminoxide. Both in the hydrated and anhydrous states it melts and decomposes at 199°, and has $[a]_D$ $-1·75°$. It is moderately soluble in cold water (at 22°, 10 c.c. of a saturated solution contain 0·1864 gram of anhydrous oxide); the solution is neutral and has a bitter taste. The oxide is insoluble in ether or light petroleum. It evolves oxygen when gently warmed, and liberates iodine from potassium iodide in the cold. Strychnine sulphate is formed when sulphur dioxide is passed into a concentrated aqueous solution of the oxide and the alkaloid is regenerated by the action of nitrous acid on the oxide.

The salts are sparingly soluble. The solutions are acid and do not yield precipitates with ammonia. The *hydrochloride*, $C_{21}H_{22}O_3N_2,HCl$, crystallises in long, glistening needles, darkens at 250°, but is still solid at 310°. The *platinichloride* forms flat needles and is insoluble in water. The *hydriodide* forms pale yellow, quadratic plates and melts and decomposes at 253°; it forms reddish-yellow periodides. The *nitrate* crystallises in prisms and melts and decomposes at about 250°; the *picrate* melts and decomposes at 208°; the *hydrogen sulphate* crystallises in large, four-sided plates, is somewhat more soluble in water than the other salts, and melts above 300°.

Methyl iodide reacts with the oxide yielding strychnine methiodide.

The physiological action is very similar to that of the alkaloid.

The conclusion is drawn that the nitrogen atom in strychnine to which the oxygen becomes attached must be linked to three distinct carbon atoms, and these are contained in two ring systems, since no alkyl group appears to be attached to the nitrogen (compare Freund, Abstr., 1904, i, 613). Brucine also yields a crystalline oxide.

J. J. S.

Yohimbine. II. Methylation of Yohimboaic Acid. Leopold Spiegel (*Ber.*, 1905, **38**, 2825—2833. Compare Spiegel and Auerbach, Abstr., 1904, i, 521).—The action of diazomethane on yohimboaic acid leads to the formation of yohimboaic anhydride and *yohimbine yohimboate*, which melts at 120—125° and on treatment with ammonia yields yohimbine. If an excess of diazomethane is used, the yohim-

boaic acid is converted completely into yohimbine. The *anhydride*, $C_{20}H_{24}O_3N_2$, which is formed also by the action of methyl or ethyl alcohol on the acid, crystallises from alcohol and melts at 296°; on exposure to the air, it changes into a crystalline powder which melts, when rapidly heated, at 249°. It can be recrystallised almost unchanged from hot ammonia, but if recrystallised from hot water or slowly evaporated in ammoniacal solution, yields the acid. When treated with ethyl-alcoholic hydrogen chloride, the anhydride forms a crystalline hydrochloride which, on treatment with ammonia, yields ethylyohimbine melting at 189°, but treatment with methyl-alcoholic hydrochloric acid leads to the formation of yohimbine melting at 231°.

Methylyohimboaic acid, $C_9NH_{12}\cdot CO\cdot O\cdot C_9NH_{12}Me\cdot CO_2H$, formed by the action of methyl sulphate or of methyl iodide and sodium hydroxide on yohimboaic acid in *N*-potassium hydroxide solution, separates in colourless crystals, melts at 293—294°, and is easily soluble in hydrochloric or acetic acid to form solutions from which addition of an excess of sodium hydroxide precipitates the *sodium* salt; the aqueous solution of this deposits the free acid when the walls of the glass vessel are rubbed with a rod, as does also the solution of the acid in aqueous ammonia. The ammoniacal mother liquor on concentration deposits yohimboaic acid and a *substance* which forms large crystals, melts at 254°, and is a compound of yohimboaic and methylyohimboaic acids. When treated with hydrogen chloride in alcoholic solution, methylyohimboaic acid yields on evaporation a viscous *substance* which is converted into methylyohimboaic acid when treated with sodium hydroxide. The action of ethyl sulphate on yohimboaic acid leads to the formation of *ethylyohimboaic acid*, $C_{22}H_{30}O_4N_2$, which melts at 250°. G. Y.

Chloropyrrole and Chlorotribromopyrrole. X. GIROLAMO MAZZARA and ALESSANDRO BORGO (*Gazzetta*, 1905, 35, ii, 19—27. Compare this vol., i, 659).—2-*Chloro*-3 : 4 : 5-*tribromo*-1-*methylpyrrole*, $NMe<\begin{matrix}CCl:CBr\\ \quad\ \ |\\ CBr:CBr\end{matrix}$, obtained by the action of methyl-alcoholic potassium hydroxide and methyl iodide on a methyl-alcoholic solution of chlorotribromopyrrole, crystallises from alcohol in long, faintly pearly-grey needles melting at 138°, and is stable towards the action of light. On oxidation with concentrated nitric acid, it yields dibromomaleinmethylimide, so that chlorotribromopyrrole and also chloropyrrole must have the chlorine atom in the 2-position. T. H. P.

Action of Sulphuryl Chloride on Methyl Pyrrole-2-carboxylate. XI. GIROLAMO MAZZARA and ALESSANDRO BORGO (*Gazzetta*, 1905, 35, ii, 104—111).—*Methyl pyrrole-2-carboxylate*,

$$NH<\begin{matrix}CH=\!=\!=CH\\ \qquad\qquad |\\ C(CO_2Me):CH\end{matrix},$$

prepared from the corresponding ammonium salt obtained by heating together ammonium carbonate, pyrrole, and water under pressure, crystallises in shining, white needles melting at 73°.

Methyl-3 : 4 : 5-*trichloropyrrole*-2-*carboxylate*, $NH<\begin{matrix}CCl{=\!=\!=}CCl \\ C(CO_2Me){:}CCl\end{matrix}$, prepared by the action of sulphuryl chloride (3 mols.) on an ethereal solution of methyl pyrrole-2-carboxylate (1 mol.), crystallises from alcohol in shining, white needles melting at 189° and is soluble in light petroleum. It is accompanied by *methyl dichloropyrrole*-2-*carboxylate*, $C_4NH_2Cl_2{\cdot}CO_2Me$, which can be obtained pure by using two mols. of sulphuryl chloride and one of methyl pyrrole-2-carboxylate; it crystallises from light petroleum in slender needles melting at 132—134° and dissolves in water or alcohol.

Methyl chloropyrrole-2-*carboxylate*, $C_4NH_3Cl{\cdot}CO_2Me$, prepared by the interaction of sulphuryl chloride and methyl pyrrole-2-carboxylate in molecular proportions, was not obtained pure, but melts at about 90°. The corresponding *acid*, $C_4NH_3Cl{\cdot}CO_2H$, separates from water in faintly rose-coloured crystals which soften and decompose at about 130°. T. H. P.

Cyclic Bases from Methylheptenone. OTTO WALLACH (*Ber.*, 1905, **38**, 2803—2806).—The additive compound of the base $C_8H_{15}N$ and benzaldehyde (Abstr., 1902, i, 81) appears to be a benzhydrol, $C_8H_{14}N{\cdot}CHPh{\cdot}OH$, as it slowly decomposes into its components.

[With PETROS RHOUSSOPOULOS.]—Methylheptenylamine combines with two molecules of hydrogen chloride or bromide, and the products, when distilled, yield a *hydrocarbon*, C_8H_{14}, boiling at 130°, and a base, $CHMe_2{\cdot}CH<\begin{matrix}CH_2{\cdot}CH_2 \\ NH{-}CHMe\end{matrix}$ (?), isomeric with coniine. This distils at 150—151°, has a specific gravity 0·823, and n_D 1·4398 at 20°. The *hydrochloride* melts at 218—220° and the *platinichloride* at 221—223°. The *nitrosoamine* distils at 114° under 10 mm. pressure, and the *sulphonamide*, $C_8H_{16}N{\cdot}SO_2Ph$, melts at 76—78°. When completely methylated, it yields a *quaternary ammonium iodide*, $C_8H_{16}NMe_2I$, which melts at 242—243°.

Attention is drawn to the fact that a similar decomposition to that described by Lipp and Widnmann (this vol., i, 610) has been previously observed with the base $C_8H_{15}N$. J. J. S.

4-Stilbazole and 3′-Nitro-4-stilbazole. KONRAD FRIEDLÄNDER (*Ber.*, 1905, **38**, 2837—2840. Compare this vol., i, 232).—*Dihydro*-4-*stilbazole*, $C_5NH_4{\cdot}CH_2{\cdot}CH_2Ph$, formed by heating 4-stilbazole with fuming hydriodic acid and red phosphorus in a sealed tube at 150°, crystallises in white needles and melts at 65°. The *hydrochloride*, $C_{13}H_{13}N,HCl$, melts at about 180°; the *hydriodide* crystallises in glistening, brown leaflets and decomposes at 150°; the *aurichloride*, $C_{13}H_{13}N,HAuCl_4$, forms leaflets and melts at 166°; the *platinichloride*, $(C_{13}H_{13}N)_2,H_2PtCl_6$, forms brown leaflets and commences to melt slowly at 214°.

4-*Stilbazoline*, $C_5NH_{10}{\cdot}CH_2{\cdot}CH_2Ph$, prepared by reduction of 4-stilbazole with sodium in alcoholic solution, forms a light oil which has an unpleasant odour and boils at 200—210° under 80 mm. pressure. The *aurichloride*, $C_{13}H_{19}N,HAuCl_4$, forms golden-red leaflets and melts

and decomposes at 204°; the *platinichloride*, $(C_{13}H_{19}N)_2,H_2PtCl_6$, forms brown leaflets and melts at about 210°.

3'-Nitro-4-stilbazole, $C_5NH_4·CH:CH·C_6H_4·NO_2$, formed by heating *m*-nitrobenzaldehyde and 4-methylpyridine in a sealed tube at 180—200°, crystallises from alcohol in brown needles and melts at 138°. The *hydrochloride*, $C_{13}H_{10}O_2N_2,HCl$, is a white powder melting at 221—222°; the *picrate* forms explosive, yellowish-green crystals; the *platinichloride*, $(C_{13}H_{10}O_2N_2)_2,H_2PtCl_6$, crystallises in reddish-yellow leaflets and melts at a high temperature; the *aurichloride* forms a red powder and melts at a high temperature. Reduction of 3'-nitro-4-stilbazole with stannous chloride in alkaline solution leads to the formation of *azo-4-stilbazole*, $N_2(C_6H_4·CH:CH·C_5NH_4)_2$, which forms small, red crystals and melts at 220—221°. 3'-Nitro-4-stilbazole is reduced electrolytically in concentrated sulphuric acid with a current density of $2\frac{1}{2}$—3 amperes and an *E.M.F.* of 4 volts, with formation of *3'-amino-6'-hydroxy-4-stilbazole*, $C_5H_4N·CH:CH·C_6H_3(NH_2)·OH$, which separates from alcohol in small, glistening prisms and melts at 123°. *3'-Aminodihydro-4-stilbazole*, $C_5NH_4·CH_2·CH_2·C_6H_4·NH_2$, is formed by reduction of 3'-nitro-4-stilbazole with fuming hydriodic acid and red phosphorus at 135—150°, or with tin and hydrochloric acid. It crystallises from alcohol in almost colourless needles and melts at 127—129°. G. Y.

β-Aminotricarballylic Acid. GEORG SCHROETER (*Ber.*, 1905, 38, 3181—3189. Compare Schroeter and Kirnberger, Abstr., 1902, i, 531).—[With R. SCHWAMBORN and C. STASSEN.]—*β-Anilinotricarballylic acid*, $NHPh·C(CH_2·CO_2H)_2·CO_2H,H_2O$, is formed by boiling the ethyl ester of its imide (*loc. cit.*) with 12 per cent. aqueous sodium hydroxide and adding a limited quantity of hydrochloric acid to the product; if more dilute sodium hydroxide is used, the hydrolysis proceeds further with formation of aniline. The anilino-acid is obtained as a crystalline powder, melts and decomposes at 161—162°, or, after losing H_2O at 90° under reduced pressure, at 169°, and is slowly hydrolysed by boiling 10 per cent. hydrochloric acid with formation of aniline and probably aconitic acid. It neutralises almost three mols. of sodium hydroxide when titrated with phenolphthalein as indicator, but acts as a dibasic acid towards litmus in dilute solution; the concentrated solution of the *sodium* salt yields *precipitates* with salts of calcium, barium, or the heavy metals; on analysis, the *silver* and *barium* salts gave results corresponding with between two and three equivalents of metal per mol. of the acid.

The *imide* of aconitic acid, $\begin{matrix} NH·CO \\ | \\ CO·CH \end{matrix}\!\!>\!C·CH_2·CO_2H$, is formed by boiling the ethyl ester of β-anilinotricarballylimide with 2*N*-hydrochloric acid in a reflux apparatus. It crystallises from hot water, melts at 191°, and neutralises more than one mol. of sodium hydroxide when titrated with phenolphthalein as indicator, but acts as a monobasic acid towards a mixture of potassium iodide and iodate; when boiled with aqueous sodium hydroxide, it is hydrolysed with formation of ammonia and aconitic acid. The *silver* salt, $C_6H_3O_4NAg_2$, was

analysed. This substance is the *as*-imide as compared with citrazinic acid, $NH<\substack{CO\cdot CH_2 \\ CO-CH}>C\cdot CO_2H$, which is the *s*-imide of aconitic acid.

When boiled with hydrochloric acid, α-anilino-α-methylsuccinimide is hydrolysed with formation of citraconanil and a *substance* which melts at 145°.

[With R. Schwamborn.]—A molecular mixture of ethyl acetonedicarboxylate and phenetidine interacts in two days to form *ethyl phenetidil-acetonedicarboxylate*, $OEt\cdot C_6H_4\cdot N:C(CH_2\cdot CO_2Et)_2$, which crystallises from light petroleum in transparent prisms and melts at 57°. This dissolves in absolute hydrogen cyanide and, if after two to three days the excess of hydrogen cyanide is distilled off, forms the *nitrile*, $OEt\cdot C_6H_4\cdot NH\cdot C(CH_2\cdot CO_2Et)_2\cdot CN$, which, when dissolved in cold concentrated sulphuric acid, is hydrolysed to the *amide*,

$$OEt\cdot C_6H_4\cdot NH\cdot C(CH_2\cdot CO_2Et)_2\cdot CO\cdot NH_2.$$

This crystallises from aqueous alcohol or from a mixture of chloroform or benzene and light petroleum and melts at 77°. Prolonged action of concentrated sulphuric acid on the nitrile leads to the formation of the *imide*, $\begin{array}{l}OEt\cdot C_6H_4\cdot NH\cdot C(CH_2\cdot CO_2Et)\cdot CO \\ \qquad\qquad\quad CH_2 \text{———————} CO\end{array}>NH$, which crystallises from alcohol, melts at 133—134°, and has stronger basic properties than has the imide of ethyl β-anilinotricarballylate. If the imide is dissolved in aqueous sodium hydroxide and the solution carefully acidified, the *imide-acid*, $\begin{array}{l}OEt\cdot C_6H_4\cdot NH\cdot C(CH_2\cdot CO_2H)\cdot CO \\ \qquad\qquad\quad CH_2 \text{———————} CO\end{array}>NH$, is precipitated; it crystallises from water, melts and decomposes at 153°, and forms a *disodium* salt, $C_{14}H_{14}O_5N_2Na_2$. *β-Phenetidinotricarballylic acid*, $OEt\cdot C_6H_4\cdot NH\cdot C(CH_2\cdot CO_2H)_2\cdot CO_2H,2H_2O$, is formed along with a small amount of phenetidine by boiling the imide-ester with 2*N*-sodium hydroxide; it crystallises from water in small cubes, melts and decomposes at 121—122°, and loses $2H_2O$ at 55° under reduced pressure. When boiled with 2*N*-hydrochloric acid, the ethyl ester of β-phenetidinotricarballylimide is hydrolysed to phenetidine and the *as*-imide of aconitic acid.

[With C. Stassen.]—The following substances have been prepared from the toluidines in the same manner as the preceding; the temperatures given are melting points:

	o.	*m.*	*p.*
Ethyl toluidilacetonedicarboxylates	78°	59°	52°
The amides, $C_7H_7\cdot NH\cdot C(CH_2\cdot CO_2Et)_2\cdot CO\cdot NH_2$	141—142°	104°	79—80°
The imides, $\begin{array}{l}C_7H_7\cdot NH\cdot C(CH_2\cdot CO_2Et)\cdot CO \\ \qquad\quad CH_2 \text{—————} CO\end{array}>NH$	90·5—91·5°	135—136°	208—209°

The imide from *m*-toluidine is hydrolysed by sodium hydroxide with formation of m-*toluidinocarballylic acid*, which melts and decomposes at 152°, or by boiling hydrochloric acid with formation of *m*-toluidine and the *as*-imide of aconitic acid. The product obtained by treating with sulphuric acid the nitrile formed by condensation of ammonia, ethyl acetonedicarboxylate, and hydrogen cyanide is soluble in aqueous alkali hydroxides, and in neutral solution forms precipitates with solutions of

barium, copper, and silver salts. The *silver* salt so obtained gives on analysis results corresponding with a mixture of di- and tri-silver β-aminotricarballylates. G. Y.

Piperidoethyl Ether. LUDWIG KNORR, H. HÖRLEIN, and PAUL ROTH (*Ber.*, 1905, **38**, 3141—3142. Compare preceding abstract).—*Piperidoethyl ether hydrochloride*, $C_5NH_{10}\cdot CH_2\cdot CH_2\cdot OEt,HCl$, is formed along with diethylenedipiperidinium chloride when 1-chloroethylpiperidine is boiled with alcohol (compare Marckwald and Frobenius, Abstr., 1902, i, 24). The free *base*, $C_9H_{19}ON$, can be prepared by heating 1-chloroethylpiperidine hydrochloride with sodium ethoxide in alcoholic solution in a sealed tube; it forms an oil which boils at 196° under 760 mm. pressure. The *aurichloride*, $C_9H_{19}ON,HAuCl_4$, forms an oil which rapidly crystallises and melts at about 85°; the *platinichloride* crystallises in flat, monoclinic prisms and melts at 116—117°; the *picrate* is an oil; the *picrolonate* crystallises in characteristic, fan-like aggregates of leaflets. G. Y.

Simple Method for the Preparation of Pyridine Perchromate for Demonstration Purposes. KARL A. HOFMANN and H. HIENDLMAIER (*Ber.*, 1905, **38**, 3066—3067. Compare Wiede, Abstr., 1898, ii, 28).—Pyridine perchromate, CrO_5H,C_5H_5N, may be prepared by the following method. Chromic anhydride (4 grams) is dissolved in water (150 c.c.) and mixed with pyridine (9 c.c.). To this solution, which is kept cool by a good freezing mixture, 30 per cent. hydrogen peroxide (4 c.c.) dissolved in water (20 c.c.) is added. The perchromate separates as dark blue, glistening needles, practically insoluble in water, but dissolves readily in ether or glacial acetic acid. J. J. S.

Synthesis of Pyridine Compounds from β-Keto-esters and Ethyl Cyanoacetate in presence of Ammonia or Amines. II. ICILIO GUARESCHI [and, in part, with ADALBERTO PASQUALI, GALEAZZO PICCININI, GIOVANNI ISSOGLIO, and ENRICO QUENDA] (*Chem. Centr.*, 1905, ii, 681—685; from *Estr. Mem. Reale Accad. Sci. Torino*, ii, **55**. Compare Abstr., 1897, i, 168).—When treated with ammonia, β-ketonic esters (1) containing the alkyl group, C_nH_{2n+1}, yield amino-esters, $C_nH_{2n+1}\cdot C(NH_2)\colon C(C_nH_{2n+1})\cdot CO_2C_nH_{2n+1}$, and β-ketoamides, $C_nH_{2n+1}\cdot CO\cdot CH(C_nH_{2n+1})\cdot CO\cdot NH_2$; (2) having an aromatic group attached to the carbonyl, yield amino-amides such as

$$NH_2\cdot CPh\colon CH\cdot CO\cdot NH_2,$$

and β-keto-amides such as $CH_2Bz\cdot CO\cdot NH_2$, which are easily formed from the amino-amides (compare Abstr., 1904, i, 891); (3) containing an aromatic alkyl group, such as ethyl benzylacetoacetate, yield the corresponding β-keto-amides, such as $CH_2Ph\cdot CHAc\cdot CO\cdot NH_2$, and small amounts of the amino-esters, as $NH_2\cdot CMe\colon C(CH_2Ph)\cdot CO_2Et$; (4) derived from dibasic acids, yield the amino-imides, such as $NH_2\cdot CMe\colon C{<}\begin{matrix}CO\text{—}NH\\ CH_2\cdot CO\end{matrix}$, and the β-keto-amides, such as

$$NH_2\cdot CO\cdot CH_2\cdot CHAc\cdot CO\cdot NH_2,$$

from ethyl acetosuccinate. The β-keto-amides react with ethyl cyanoacetate to form generally dihydroxypyridines.

The *ammonium* compound of cyanomethylpropylglutaconimide (3-cyano-2 : 6-diketo-4-methyl-5-*n*-propyl-Δ^3-tetrahydropyridine),

$$C_{10}H_{11}O_2N_2,NH_4,$$

obtained by the action of ammonia on ethyl *n*-propylcyanoacetate and ethyl cyanoacetate, crystallises from water, gives a bluish-violet coloration with ferric chloride, a yellow, crystalline precipitate with copper acetate, and a white precipitate with silver nitrate. The free base, $CMe{<}{\begin{array}{l}C(CN)\cdot CO\\ CHPr^{\alpha}\cdot CO\end{array}}{>}NH$, forms small crystals, melts at 221—222°, gives a violet coloration with alcoholic ferric chloride, and when heated yields γ-cyano-β-methyl-α-propylvinylacetic acid. n-*Propylacetoacetamide*, $C_7H_{13}O_2N$, crystallises in long, glistening needles, melts at 105—106°, gives a blue coloration with ferric chloride, and reacts with ammonia and cyanoacetamide in aqueous solution to form cyanomethyl-*n*-propylglutaconimide. Ethyl β-amino-α-*n*-propylcrotonate crystallises in large, glistening leaflets, melts at 44—45°, has a strong odour of peppermint, and becomes yellow on exposure to air. The corresponding *iso*propyl compounds were obtained only in small quantities.

The *ammonium* derivative of cyanomethyl*iso*butylglutaconimide, $\begin{array}{l}CH_2Pr^{\beta}\cdot CH\cdot CMe{:}C\cdot CN\\ NH_4\cdot O\cdot C{:}N\text{———}CO\end{array}$ or $\begin{array}{l}CH_2Pr^{\beta}\cdot CH\cdot CMe{=\!=}C\cdot CN\\ CO\cdot N(NH_4)\cdot CO\end{array}$, crystallises from water, gives a bluish-violet coloration with ferric chloride, forms white precipitates with silver nitrate and barium chloride, and with cobalt nitrate a rose-coloured precipitate consisting of needles. The yellow precipitate formed with copper sulphate becomes red on addition of more of the reagent, and changes slowly at the ordinary temperature, quickly when warmed, into the yellow anhydrous salt,

$$(C_{11}H_{13}O_2N_2)_2Cu\,;$$

with copper acetate there is formed the salt $Cu{<}{\begin{array}{l}CBu^{\beta}\cdot CMe{:}C\cdot CN\\ CO{:}N\text{———}CO\end{array}}$ or $\begin{array}{l}C(CN){:}CMe\cdot CBu^{\beta}\text{—}Cu\cdot CBu^{\beta}\cdot CMe{:}C\cdot CN\\ CO\cdot N{=\!=\!=}C\cdot O\cdot Cu\cdot O\cdot C{:}N\text{———}CO\end{array}$. The ammonium salt gives crystalline precipitates also with quinine and cinchonine sulphates and benzylamine and ethylenediamine hydrochlorides. iso*Butylacetoacetamide*, $CH_2Pr^{\beta}\cdot CHAc\cdot CO\cdot NH_2$, crystallises in colourless needles, melts at 92°, and gives a violet coloration with ferric chloride. *Ethyl amino*iso*butylacetoacetate*, $NH_2\cdot CMe{:}CBu^{\beta}\cdot CO_2Et$, is crystalline and melts at 42—43°. The *ammonium* derivative of cyanomethyl-*n*-butylglutaconimide forms colourless crystals, gives an intense bluish-violet coloration with ferric chloride, and forms a scarlet precipitate which becomes yellow with copper sulphate, white precipitates with silver nitrate and calcium and barium chloride, a rose-coloured precipitate consisting of rhombohedra or sheaves of needles, a green precipitate with nickel nitrate, and precipitations with quinine and cinchonine sulphates and benzylamine hydrochloride.

n-*Butylacetoacetamide*, $C_8H_{15}O_2N$, crystallises in needles, melts at 116—117°, and gives a bluish-violet coloration with ferric chloride. *Ethyl amino*-n-*butylacetoacetate*, $NH_2\cdot CMe{:}CBu^{\alpha}\cdot CO_2Et$, forms a white, crystalline mass having an odour of peppermint.

The prolonged action of ammonia on ethyl *iso*amylacetoacetate leads to the formation of only a small amount of *ethyl amino*iso*amylacetoacetate*, which has an odour of camphor. The *ammonium* derivative of cyanomethylallylglutaconimide gives an intense blue coloration with aqueous ferric chloride. The *copper* derivative is yellow, the *silver* derivative forms a white precipitate, the *barium* derivative crystallises in short prisms. The free *base*, $CMe{<}{\scriptstyle C(CN)\text{——}CO \atop \scriptstyle CH(C_3H_5)\cdot CO}{>}NH$ or

$$CMe{<}{C(CN)\text{———}CO \atop CH(C_3H_5)\cdot C(OH)}{\geqslant}N,H_2O,$$

crystallises from water, loses H_2O at 99—100°, becomes blue at 100—110°, and melts at 172—173°. In aqueous solution, the base becomes violet when exposed to the air, forms a crystalline compound with bromine, gives a bluish-green coloration with nitrous acid, and is converted by concentrated sulphuric acid into cyanoallylvinylacetic acid. The action of ethyl hydroxyethylacetoacetate and ammonia on ethyl cyanoacetate leads to the formation of the *compound*,

$$CMe{<}{C(CN)\text{————}CO \atop CH(CH_2\cdot OH)\cdot C(OH)}{\geqslant}N,$$

which crystallises in colourless or yellow needles, has a slight acid reaction in aqueous solution, gives a violet coloration with ferric chloride or when boiled with bromine water, and forms a *potassium* derivative crystallising in glistening needles. *Benzylacetoacetamide*, $CH_2Ph\cdot CHAc\cdot CO\cdot NH_2$, is the principal product of the interaction of ethyl benzylacetoacetate, ethyl cyanoacetate, and ammonia. It crystallises in thick needles, melts at 150—151°, gives a violet coloration with alcoholic ferric chloride, and evolves ammonia when boiled with 20 per cent. potassium hydroxide solution.

Cyanobenzylmethylglutaconimide (5-*cyano*-6-*keto*-2-*hydroxy*-3-*benzyl*-4-*methyl*-3 : 6-*dihydropyridine*), $C_{14}H_{12}O_2N_2,H_2O$, crystallises in short, colourless, glistening prisms, loses H_2O at 100—110°, becomes brown at 215°, melts at 217—218°, gives a bluish-violet coloration with alcoholic ferric chloride, and when boiled with 60 per cent. sulphuric acid yields cyanobenzylmethylvinylacetic acid. The *ammonium*, $C_{14}H_{11}O_2N_2,NH_4$, *barium, calcium, magnesium* ($9H_2O$), *silver, copper, quinine, cinchonine*, and *strychnine* derivatives are described.

5-*Cyano*-2 : 6-*diketo*-4-*methyl*-Δ^4-*tetrahydropyridyl*-3-*acetic acid*,

$$CO_2H\cdot CH_2\cdot CH{<}{CMe{:}C(CN) \atop C(OH)=N}{>}CO$$

or $CO_2H\cdot CH_2\cdot CH{<}{\scriptstyle CMe{:}C(CN) \atop \scriptstyle CO\text{——}NH}{>}CO$, crystallises in colourless needles, melts at 202°, and gives an intense blue coloration when warmed with 5 per cent. potassium nitrite solution, a red coloration with bromine water, and a dark violet precipitate with ferric chloride. The *di-ammonium*, $C_7H_4ON_2(ONH_4)\cdot CH_2\cdot CO_2NH_4$, *mono-ammonium*, $C_7H_5O_2N_2\cdot CH_2\cdot CO_2NH_4$, *barium*, $C_9H_6O_4N_2Ba,2H_2O$, *silver*, $C_9H_7O_4N_2Ag,H_2O$, and *di-silver*, $C_9H_6O_4N_2Ag_2$, salts are described.

β-Aminocinnamamide, $NH_2\cdot CPh{:}CH\cdot CO\cdot NH_2$, crystallises from water in glistening leaflets, melts at 164·5—165°, and gives a rose coloration with nitrous fumes in sulphuric acid solution, and a rose-violet

with alcoholic or aqueous ferric chloride. *Cyanophenylglutaconimide*, $C_{18}H_8O_2N_2,H_2O$, crystallises in needles, loses H_2O at 100—110°, becomes brown at 265—270°, and melts at about 285°. It gives a green coloration with potassium nitrite and sulphuric acid and a red with bromine water, and when treated with 60 per cent. sulphuric acid is converted into γ-cyano-β-phenylvinylacetic acid. The *ammonium, magnesium, barium* ($5H_2O$), and *copper* salts are described.

G. Y.

Reduction of 4-Methyl-3-ethylpyridine with Sodium and Alcohol. Wilhelm Koenigs and Karl Bernhart (*Ber.*, 1905, **38**, 3042—3049).—β-Collidine or 4-methyl-3-ethylpyridine (Koenigs, Abstr., 1894, i, 477), when reduced with excess of sodium and absolute ethyl alcohol, yields a mixture of a tetrahydro- and a hexahydro-derivative, which are best separated by conversion of the tetrahydro-derivative into *dibromohexahydro-β-collidine hydrobromide*,

$$C_8H_{15}NBr_2,HBr,$$

which is insoluble in cold ethyl acetate, whereas hexahydro-β-collidine hydrobromide is readily soluble. The hydrobromide crystallises in slender needles, melts and decomposes at 163—164°, and is optically inactive. The dibromo-derivative itself has been obtained only as a resin with an odour of camphor. With nitrous acid, the hydrobromide yields a *nitroso*-derivative melting at 107—108°. Tetrahydro-β-collidine, obtained by the action of zinc dust and sulphuric acid on the hydrobromide, distils at 177° under 719 mm. pressure, and yields an *acid tartrate* melting at 165—167°. From this a normal *oxalate*, $C_{18}H_{32}O_4N_2$, melting and decomposing at 199°, has been prepared; it is optically inactive. The *carbonate* melts at 60—62°. The *aurichloride*, $C_8H_{15}N,HAuCl_4$, crystallises in yellow plates, melts at 148—149°, and is sensitive to light. The *platinichloride* melts and decomposes at 194° and the *picrate* melts at 127—128°. The pure base immediately decolorises permanganate.

Hexahydro-β-collidine hydrogen tartrate crystallises in colourless needles and melts and decomposes at 194—195°. The normal *oxalate* melts at 185—187°. The hydrochloride dissolves readily in water, the *aurichloride* crystallises from a mixture of alcohol and ether in yellow needles melting at 126—128°. The *platinichloride* melts and decomposes at 208°. The base does not decolorise acidified permanganate, and with a chloroform solution of bromine yields a perbromide.

J. J. S.

3 : 4-Diethylpyridine, 3 : 4-Diethylpiperidine, and 3-Ethylquinuclidine. Wilhelm Koenigs and Karl Bernhart (*Ber.*, 1905, **38**, 3049—3057. Compare Abstr., 1904, i, 925).—3 : 4-*Diethylpyridine* is obtained when 3-ethylpyridyl-4-ethanol (Abstr., 1902, i, 395) is reduced with hydriodic acid and red phosphorus and, after removal of the phosphorus, treated with zinc dust in a freezing mixture and kept overnight. The base, after purification by means of the picrate, distils at 207—209° under 710 mm. pressure. The *aurichloride*, $C_9H_{13}N,HAuCl_4$, crystallises from dilute hydrochloric acid in slender, yellow needles and melts at 111—112°. The *platinichloride* crystal-

lises in orange-red plates, melting and decomposing at 221°. The *mercurichloride* forms colourless needles melting at 90—98°. The *picrate* forms slender needles sparingly soluble in water and melts at 139°.

When reduced with sodium and alcohol, part of the base is transformed into 3 : 4-diethylpiperidine, but unaltered base and its tetrahydro-derivative are also present. 3 : 4-*Diethylpiperidine* is most readily obtained from methylolhexahydro-β-collidine,

$$OH\cdot CH_2\cdot CH_2\cdot C_5H_9EtN.$$

The aurichloride of this melts at 124—126°. When the free base is reduced with hydriodic acid and red phosphorus, it yields the *hydriodide*, $CH_2I\cdot CH_2\cdot C_5H_9EtN,HI$. This crystallises from ice-cold water, melts at 96°, is readily soluble and, on reduction with zinc dust and hydriodic acid at low temperatures, yields 3 : 4-diethylpiperidine. The base distils at 193° under 720 mm. pressure, the *hydrochloride* crystallises from ethyl acetate in colourless needles melting at 107—108°. The *platinichloride* melts at 159—160°, the *aurichloride* at 120—130°, the *hydrobromide* at 102—103°, and the *picrate* at 107—108°. The *phenylcarbimide* derivative crystallises from light petroleum and melts at 87—88°; the p-*nitrotoluenesulphone* derivative,

$$C_5H_8Et_2N\cdot SO_2\cdot C_6H_3Me\cdot NO_2,$$

crystallises from alcohol and melts at 89—90°. The corresponding derivative of piperidine melts at 85°.

The hydriodide, melting at 96°, yields β-ethylquinuclidine, identical in all respects with the compound already described (Abstr., 1904, i, 925). Its properties are those of a tertiary base, and the methiodide melts at 130° and shows all the properties of a quaternary ammonium iodide. The base is extremely stable, is not decomposed by dilute hydrochloric acid at 170—180°, by phosphoric acid at 190—200°, by fuming hydrobromic acid at 190—200°, or by alcoholic potash. It appears to combine with bromine, yielding a colourless additive compound melting at 152°, and this with sulphurous acid yields the unaltered base. J. J. S.

2-Methyl-6-pyrophthalone. A. SCHOLZE (*Ber.*, 1905, **38**, 2806—2809. Compare Huber, Abstr., 1903, i, 576; Gaebelé, *ibid.*, 1904, i, 88).—2-*Methyl*-6-*pyrophthalone*, $C_5NH_3Me\cdot CH\colon C<\substack{O\\C_6H_4}>CO$, is obtained when phthalic anhydride, 2 : 6-dimethylpyridine (Ahrens, this vol., i, 232), and a fragment of zinc chloride are heated for eight hours at 170°. It crystallises from alcohol, by spontaneous evaporation, in deep bluish-red needles melting at 210—211°, is soluble in most organic solvents and in concentrated hydrochloric acid. Most of the salts dissolve readily in alcohol, chloroform, or acetic acid, and melt at about 210° owing to dissociation. The following have been prepared: *hydrochloride*, $C_{15}H_{11}O_2N,HCl$, *hydrobromide*, *platinichloride*, *mercurichloride*, and *sodium* salt, $C_5NH_3Me\cdot CNa\colon C<\substack{O\\C_6H_4}>CO$.

It has not been found possible to condense the pyrophthalone with a further quantity of phthalic anhydride. J. J. S.

Preparation of New Polymethyleneimines by Ladenburg's Method. Michael I. Konowaloff and S. Woinitsch-Sianoschensky (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 523—530).—On subjecting small quantities of *s*-tetramethyltetramethylenediamine ($NH_2\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CMe_2\cdot NH_2$) hydrochloride to dry distillation and collecting the distillate in hydrochloric acid, an oily mixture of the hydrocarbons, C_8H_{16} and C_8H_{14}, having the boiling point 130—135° at 754 mm. pressure and a sp. gr. 0·772 at 0° and 0·759 at 17·5°, is obtained, together with a mixture of bases from which was isolated the *benzoyl* derivative, $C_8H_{16}NBz$, melting at 67·5—68°, of 2 : 2 : 5 : 5-tetramethylpyrrolidine (2 : 2 : 5 : 5-tetramethyltetramethyleneimine), $\begin{matrix} CH_2\cdot CMe_2 \\ | \\ CH_2\cdot CMe_2 \end{matrix}\!\!>\!NH$.

Similarly, dry distillation of *s*-tetramethylhexamethylenediamine ($NH_2\cdot CMe_2\cdot [CH_2]_4\cdot CMe_2\cdot NH_2$) hydrochloride yields: (1) a mixture of unsaturated hydrocarbons, $C_{10}H_{20}$ and $C_{10}H_{18}$; (2) a mixture of bases from which was isolated 2 : 2 : 7 : 7-*tetramethylhexamethyleneimine*,

$$\begin{matrix} CH_2\cdot CH_2\cdot CMe_2 \\ | \\ CH_2\cdot CH_2\cdot CMe_2 \end{matrix}\!\!>\!NH,$$

which forms a very stable hydrate, $C_{10}H_{21}N,H_2O$, melting at 36—36·5°, boiling at 236·5—237° under 749 mm. pressure, and having a sp. gr. 0·87913 at 16°/0° and n_D 1·45782 at 16°; the anhydrous base (?) melts at 140·5—141° and readily combines with water; the *benzoyl* derivative, $C_{10}H_{20}NBz,H_2O$, crystallises from light petroleum in silky needles melting at 76·5—77°, and dissolves readily in alcohol or benzene. The following salts of 2 : 2 : 7 : 7-tetramethylhexamethyleneimine were prepared: the *oxalate*, melting at 226°; the *hydrobromide*, melting at 149°; the *sulphate*, *nitrate*, and *auribromide*; the *picrate*, melting at 117·5—118°. T. H. P.

Synthesis of Hexamethyleneimine—the Cyclic Homologue of Piperidine. Julius von Braun and Adolf Steindorff (*Ber.*, 1905, **38**, 3083—3094).—ζ-*Phenoxyhexylamine*, $OPh\cdot[CH_2]_6\cdot NH_2$, is obtained by the reduction of the nitrile of phenoxyhexoic acid (this vol., i, 207, 342) with sodium and alcohol. It can be isolated by means of its sparingly soluble *hydrochloride*, which crystallises from its aqueous solution in compact prisms melting at 140°. The base is a colourless oil distilling at 167—169°; it has a faint basic odour and solidifies when cooled with ice. The *platinichloride* forms yellowish-red crystals from water, turns black at 191°, and is molten at 199°. The *picrate* melts at 135°; the *benzoyl* derivative,

$$OPh\cdot[CH_2]_6\cdot NH\cdot COPh,$$

crystallises from dilute alcohol and melts at 80°, and the *benzenesulphonyl* derivative, $OPh\cdot[CH_2]_6\cdot NH\cdot SO_2Ph$, melts at 57—58°. In the presence of alkali hydroxide, the base readily absorbs carbon dioxide, yielding the sparingly soluble *sodium phenoxyhexylcarbamate*, $OPh\cdot[CH_2]_6\cdot NH\cdot CO_2Na$, which crystallises in glistening plates. It melts at 80°, at the same time evolving carbon dioxide and leaving a wax-like residue of the *sodio-amide*, $OPh\cdot[CH_2]_6\cdot NHNa$, which is decomposed by water into phenoxyhexylamine and sodium hydroxide.

ζ-Chlorohexylamine (this vol., i, 635) is formed when the phenoxy-compound is heated with four times its weight of concentrated hydrochloric acid at 90°. The corresponding *ζ-bromohexylamine* is prepared by heating the phenoxy-derivative at 80° with hydrobromic acid saturated at 0°. The *hydrobromide* is hygroscopic, and the *picrate* melts at 127° and dissolves sparingly in water. The chloro- and bromo-bases are stable at low temperatures, but when heated alone or in presence of water they yield *hexamethyleneimine* salts and their polymerides. For the preparation of hexamethyleneimine, it is not necessary to use the pure base; the product of decomposition of the phenoxy-compound with hydrobromic acid is freed from phenol, made alkaline, and distilled in steam. The yield of base is some 10 per cent. It is a mobile liquid, miscible with water, has an odour like piperidine, and distils at about 120—130°. The *hydrochloride* has been obtained in the form of a syrup only; the *platinichloride* crystallises in reddish-yellow needles, melting and decomposing at 148—149°. The *aurichloride* and *picrate* are obtained as red oils which slowly solidify. The *benzenesulphonyl* derivative is an oil and is insoluble in water. When completely methylated, the base yields the *quaternary ammonium iodide*, $\begin{matrix} CH_2\cdot CH_2\cdot CH_2 \\ | \\ CH_2\cdot CH_2\cdot CH_2 \end{matrix}\!\!>\!NMe_2I$, which melts at 214—215°. The corresponding *platinichloride* melts between 245° and 255°.

The polymeric base, $(C_6NH_{13})_n$, is not volatile with steam, and forms a wax-like mass insoluble in water or ether, but soluble in chloroform or alcohol or acids. Most of the salts and derivatives are oily or pasty. The *platinichloride* is insoluble in cold water, and turns black and melts at 228°. When completely methylated, it yields a *quaternary* salt, the *platinichloride* of which dissolves extremely sparingly in water and decomposes at 255°. J. J. S.

Action of Sulphuryl Chloride on 2-Methylindole (Methylketole). GIROLAMO MAZZARA and ALESSANDRO BORGO (*Gazzetta*, 1905, **35**, ii, 100—104).—3-(?)-*Chloro-2-methylindole*,

$$CMe\!\!<\!\!\begin{matrix} CCl\cdot C\cdot CH\colon CH \\ \quad\ \ \| \qquad\quad | \\ NH\cdot C\cdot CH\colon CH \end{matrix},$$

prepared by the action of sulphuryl chloride (1 mol.) on an absolute ethereal solution of 2-methylindole (1 mol.), crystallises from light petroleum in large, shining, nacreous scales melting at 98°, and is soluble in dilute sulphuric acid, to which it imparts a feeble amethyst coloration; readily soluble in ether, and slightly so in water. It has a fæcal odour resembling that of 3-methylindole, and a pine splinter moistened with hydrochloric acid and immersed in its vapour turns red, whilst paper on which it is placed becomes first yellow and later red. When inhaled, the vapour produces nausea and dizziness.

T. H. P.

Constitution of the Indole Group in Albumin. II. Synthesis of Indole-3-propionic Acid (Nencki's Scatoleacetic Acid). ALEXANDER ELLINGER (*Ber.*, 1905, **38**, 2884—2888. Compare Abstr., 1904, i, 639).—*Ethyl propionacetalylmalonate*,

$$CH(OEt)_2\cdot CH_2\cdot CH_2\cdot CH(CO_2Et)_2,$$

is formed by heating β-chloropropionacetal with ethyl malonate and sodium ethoxide in alcoholic solution in a closed vessel at 130—140° for four hours. It is a colourless liquid which boils at 170° under 20 mm. pressure, and when heated with water at 180—190° under pressure is converted into *γ-aldehydobutyric acid*, $CHO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO_2H$; on evaporation of its solution, this is obtained as a colourless syrup which is slightly volatile in a current of steam. This was converted into the *phenylhydrazone*, boiled with 10 per cent. alcoholic sulphuric acid, and poured into water; the viscid, brown oil so obtained, on hydrolysis with alcoholic potassium hydroxide, yielded *indole-3-propionic acid*, $NH<\substack{C_6H_4\\ -CH}>C\cdot CH_2\cdot CH_2\cdot CO_2H$, which, after purification by conversion into its mercuric salt, was found to be identical with Nencki's scatoleacetic acid melting at 134°.

Indole-3-methylacetic acid, $NH<\substack{C_6H_4\\ -CH}>C\cdot CHMe\cdot CO_2H$, prepared in the same manner from aldehydo*iso*butyric acid (Perkin and Sprankling, Trans., 1889, **75**, 11), separates from water as an oil which solidifies in the cold to a mass of thick prisms, melts at 107° in aqueous solution, has an odour of scatole, and with potassium nitrite in acetic acid solution forms an oily *product* which gradually resinifies.

G. Y.

Thalleioquinine Reaction of Quinine and Jaffé's Kynurenic Acid Reaction. Hermann Führer (*Ber.*, 1905, **38**, 2713—2715). —Since not only quinine, but also cupreine, gives the thalleioquinine reaction, it appeared likely that *p*-hydroxyquinoline itself would give the reaction. The author finds that this is the case.

5 : 5-*Dichloro-6-ketoquinoline*, prepared by passing chlorine into an ice-cold solution of *p*-hydroxyquinoline hydrochloride, separates from light petroleum in prisms and melts at 58°; its *hydrochloride* melts and decomposes at 240°. The solutions of base and hydrochloride respectively in sodium carbonate and in alkali hydroxides are brown, whilst their ammoniacal solutions are green or blue.

When γ-hydroxyquinoline is evaporated to dryness with potassium chlorate and hydrochloric acid and ammonia added to the residue, a brown coloration is at first produced, and this becomes brown and then green. Jaffé's kynurenic acid reaction is accordingly applicable to γ-hydroxyquinoline. The colour-changes when *p*-hydroxyquinoline is used are similar, except that the brown coloration is not so intense, whilst with *o*-hydroxyquinoline the green coloration is very transient and the brown coloration is stable. A. McK.

Quinoline Derivatives. I. 5-Quinaldine Derivatives. Herman Decker and Percy Remfry (*Ber.*, 1905, **38**, 2773—2777. Compare E. Alber, this vol., i, 235; Doebner and Miller, Abstr., 1884, 1373; Gerdeissen, *ibid.*, 1889, 520; Marckwald, *ibid.*, 1893, i, 727).—The following generalisation is stated. On nitrating quinoline and its derivatives, the nitro-group is substituted simultaneously in the positions 5 and 8 of the benzene ring, provided no strongly positive or negative groups are present. In quinoline itself, the proportions of the two

nitro-products formed are roughly equal, but when neutral substituents such as methyl or halogen are present, one isomeride preponderates. The two products obtained on nitrating 2-methylquinoline should thus be the 5- and 8-nitro-derivatives, and the compound stated to be 7-nitro-2-methylquinoline by Doebner and Miller is shown to be the 5-nitro-2-methylquinoline.

5-*Nitro-2-methylquinoline methiodide*, $C_9H_{11}O_2N_2I$, obtained by the action of methyl sulphate and the subsequent addition of solid potassium iodide, forms orange-yellow crystals and melts at 201°. The *picrate*, $C_{17}H_{13}O_9N_5$, crystallises in yellow needles and melts at 151·5°. 5-Nitro-1-methylquinolone (Abstr., 1892, 879) is obtained when the methiodide is oxidised in alkaline solution with potassium ferricyanide, and thus the position of the nitro-group is established.

The following compounds are 5- and not 7-substituted derivatives. Cyanomethylquinoline (Rist, Abstr., 1891, 329), quinaldinesulphonic acid, β-hydroxymethylquinoline (Doebner and Miller, Abstr., 1884, 1373); the methylquinolinecarboxylic acid melting at 285°; the so-called *m*-methylquinaldine (Abstr., 1894, i, 184); methylquinolineacrylic acid (Abstr., 1886, 265), methylquinolinealdehyde (Abstr., 1889, 522), and Claus and Momberger's nitro- and amino-quinaldinecarboxylic acids (Abstr., 1898, i, 206).

In both quinoline and quinaldine syntheses, the chief product is a 5-substituted derivative (compare Rist). J. J. S.

Action of 5-Methylacridine on Benzaldehyde and *m*-Nitrobenzaldehyde. KONRAD FRIEDLÄNDER (*Ber.*, 1905, **38**, 2840—2842). —*Acridylphenylethanol*, $C_{13}H_8N{\cdot}CH_2{\cdot}CHPh{\cdot}OH$, formed by heating 5-methylacridine and benzaldehyde together in a sealed tube at 100°, crystallises in yellow needles, melts at 196—198°, does not form an additive compound with bromine, and does not distil in a current of steam. The *platinichloride*, $(C_{21}H_{17}ON)_2,H_2PtCl_6$, forms a yellow powder; the *mercurichloride*, $(C_{21}H_{17}ON)_2,H_2HgCl_4$, forms a yellow, sparingly soluble powder which melts at 212—215°.

m-*Nitrocinnamenylacridine*, $C_{13}H_8N{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}NO_2$, formed when 5-methylacridine is heated with *m*-nitrobenzaldehyde in a sealed tube at 100°, separates from alcohol as a yellow, crystalline powder, melts at 206—208°, and has an aromatic odour. The *hydrochloride*, $C_{21}H_{14}O_2N_2,HCl$, sulphate, $(C_{21}H_{14}O_2N_2)_2,H_2SO_4$, and *aurichloride*, $C_{21}H_{14}O_2N_2,HAuCl_4$, are described. The *dibromide*, $C_{21}H_{14}O_2N_2Br_2$, forms a red, crystalline powder, which becomes colourless at 200° and is not melted at 300°. G. Y.

[Bistoluene-*p*-sulphonyl-*m*-tolylenediamide.] K. OEHLER (D.R.-P. 158662).—*Bistoluene*-p-*sulphonyl*-m-*tolylenediamide*,

$$C_6H_3Me(NH{\cdot}SO_2{\cdot}C_6H_4Me)_2,$$

prepared by boiling together 1 : 2 : 4-tolylenediamine and toluene-*p*-sulphonic chloride in alcoholic solution (compare Reverdin and Crépieux, Abstr., 1902, i, 238), melts at 192—193° and closely resembles the corresponding phenylene derivative. When fused with sulphur at 240—260° in presence of an aromatic amine of high boiling point, such as benzidine or naphthylamine, yellow dyes are obtained. C. H. D.

Reduction of Hydrazones in Acid Solution. HARTWIG FRANZEN (*J. pr. Chem.*, 1905, [ii], **72**, 211—219).—When reduced with zinc dust in alcoholic acetic acid solution, phenylbenzylidenehydrazine yields aniline, benzylaniline, ammonia, benzylamine, and dibenzylamine. The reaction is explained by the following series of equations: (1) $NHPh\cdot N:CHPh + H_2 = NHPh\cdot NH\cdot CH_2Ph$; (2) $NHPh\cdot NH\cdot CH_2Ph + H_2 = NH_2Ph + CH_2Ph\cdot NH_2$; (3) $NHPh\cdot N:CHPh + H_2O = NHPh\cdot NH_2 + C_6H_5\cdot COH$; (4) $NHPh\cdot NH_2 + H_2 = NH_2Ph + NH_3$; (5) $NH_2Ph + C_6H_5\cdot COH = NPh:CHPh + H_2O$; (6) $NPh:CHPh + H_2 = NHPh\cdot CH_2Ph$; (7) $CH_2Ph\cdot NH_2 + C_6H_5\cdot COH =$

$$CH_2Ph\cdot N:CHPh + H_2O;$$

(8) $CH_2Ph\cdot N:CHPh + H_2 = CH_2Ph\cdot NH\cdot CH_2Ph$.

On reduction in the same manner, phenyl-*p*-*iso*propylbenzylidenehydrazine yields ammonia, aniline, *p*-*iso*propylphenylbenzylamine, *p*-*iso*propylbenzylamine, and di-*p*-*iso*propylbenzylamine; phenyl-*o*-hydroxybenzylidenehydrazine yields *o*-hydroxybenzylaniline; diphenylbenzylidenehydrazine yields diphenylamine, benzylamine, and dibenzylamine; benzylideneaniline yields benzylaniline, and benzylidenebenzylamine yields dibenzylamine.

Benzylamine remains unchanged when boiled in alcoholic acetic acid solution in a reflux apparatus for nine hours. No dibenzylamine was formed on boiling benzylamine with zinc acetate in alcoholic acetic acid solution or on treatment of benzylamine with zinc dust in glacial acetic acid solution. G. Y.

Action of Phenylsemicarbazide and Semicarbazide Hydrochloride on Phthalic Anhydride. FREDERICK L. DUNLAP (*J. Amer. Chem. Soc.*, 1905, **27**, 1091—1107).—When molecular proportions of phenylsemicarbazide and phthalic anhydride are heated together at 140—145°, *phthalic acid phenylsemicarbazide*,

$$CO_2H\cdot C_6H_4\cdot CO\cdot NH\cdot CO\cdot NH\cdot NHPh,$$

is produced, which crystallises from glacial acetic acid in small clusters of white, microscopic needles, melts and decomposes at 191—192°, and is slightly soluble in alcohol or water. If this substance is heated for half an hour at 180—185°, it undergoes decomposition with formation of carbon dioxide, ammonia, phenylhydrazine, phthalimide, phthalylphenylhydrazine (anilinophthalimide), and 1:4-diketo-2-phenyl-1:2:3:4-tetrahydrophthalazine. Phthalylphenylhydrazine,

$$C_6H_4{<}{}^{CO}_{CO}{>}N\cdot NHPh,$$

described by Hötte (Abstr., 1886, 353) and Pickel (Abstr., 1886, 545), crystallises in two forms, a stable yellow form and a labile white form, both melting at 179—179·5°. The stable modification can be obtained free from the labile form by crystallisation from hot glacial acetic acid, whilst the labile form is best prepared by crystallisation from alcohol. The yellow modification forms holohedral, monoclinic crystals [$a:b:c = 1\cdot1671:1:0\cdot7848$; $\beta = 54°50'$], whilst the white modification crystallises in holohedral, rhombic prisms [$a:b:c = 0\cdot2526:1:0\cdot9118$].

1:4-Diketo-2-phenyl-1:2:3:4-tetrahydrophthalazine,

$$C_6H_4{<}{}^{CO\cdot NH}_{CO\cdot NPh},$$

which was first described by Pellizzari (Abstr., 1886, 1025) under the

name of phthalylphenylhydrazide, and afterwards by Hötte (Abstr., 1887, 669), who termed it β-phthalylphenylhydrazine, crystallises in white needles and melts at 210°.

When molecular proportions of phthalimide and phenylhydrazine are heated together at 120°, anilinophthalyldiamide (Hötte, *loc. cit.*) is produced, which is decomposed by heat with formation of ammonia, phthalylphenylhydrazine, and 1 : 4-diketo-2-phenyl-1 : 2 : 3 : 4-tetrahydrophthalazine.

If a solution of phthalic anhydride (1 mol.) and phenylhydrazine (1 mol.) in chloroform is left for several hours, anilinophthalamic acid separates, which is decomposed by heat with production of phthalylphenylhydrazine and 1 : 4-diketo-2-phenyl-1 : 2 : 3 : 4-tetrahydrophthalazine, the relative proportions of these substances formed depending on the temperature.

Phthalylsemicarbazide, $C_6H_4<\substack{CO\\CO}>N{\cdot}CO{\cdot}NH{\cdot}NH_2$, obtained by heating a mixture of semicarbazide hydrochloride and phthalic anhydride at 160°, crystallises in white needles, melts and decomposes at 262°, and is slightly soluble in boiling water or alcohol. This compound is readily soluble in dilute alkali and, on acidifying the solution, *phthalic acid semicarbazide*, $CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH_2$, is precipitated, which crystallises in slender, white prisms, is soluble in alcohol or glacial acetic acid, and, when heated, is converted into phthalylsemicarbazide and then melts at 262°. E. G.

Oxazones. ROBERT GNEHM and LEO BAUER (*J. pr. Chem.*, 1905, [ii], 72, 249—277).—*Diethylaminoazobenzene*, $NEt_2{\cdot}C_6H_4{\cdot}N_2Ph$, formed by the action of phenyldiazonium nitrate on diethylaniline in aqueous sodium acetate solution, crystallises in golden leaflets or brownish-orange needles, melts at 97·8°, and dissolves in dilute acids to form red solutions. The *hydrochloride*, $C_{16}H_{20}N_3Cl$, crystallises from alcohol in flat, orange needles, forms carmine solutions, and is hydrolytically dissociated in aqueous solution; the *sulphate*, $C_{16}H_{19}N_3,H_2SO_4$, crystallises in red leaflets or slender needles, melts at 137°, forms blood-red solutions, and yields the free base when boiled with water.

p-*Tolueneazodiethylaniline*, $NEt_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_7H_7$, formed by the action of diazotised *p*-toluidine on diethylaniline, crystallises from ether or alcohol in orange leaflets and melts at 113°. The *hydrochloride*, $C_{17}H_{21}N_3,HCl$, forms thin, orange plates and melts at 179°; the *sulphate*, $C_{17}H_{21}N_3,H_2SO_4$, crystallises in red needles and melts at 179°.

a-Naphthaleneazodiethylaniline, $NEt_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_7$, crystallises in glistening, green leaflets and melts at 108°. The *hydrochloride* forms a brown, viscous resin; the *sulphate*, $C_{20}H_{21}N_3,H_2SO_4$, crystallises from alcohol in brown leaflets and melts at 189·5°.

β-Naphthaleneazodiethylaniline, formed from β-naphthylamine and diethylaniline, crystallises from light petroleum or nitrobenzene in brownish-red needles or leaflets and melts at 137·6°. The *hydrochloride*, $C_{20}H_{21}N_3,HCl$, crystallises in golden-brown leaflets and melts at 174°; the *sulphate* forms golden-brown leaflets and melts at 171°.

The yield of gallamine-blue, $C_{15}H_{13}O_4N_3,HCl$, obtained by treating gallamide in alcoholic solution with nitrosodimethylaniline, is largely

increased by using an excess of the latter, part of which undergoes reduction during the reaction. The dye forms dark green, glistening, microscopic plates, which appear blue by transmitted light, decomposes above 320°, and is easily soluble in boiling nitrobenzene or glacial acetic acid, less so in boiling water, or amyl, ethyl, or methyl alcohol, and only sparingly so in benzene, xylene, chloroform, or acetone; the solutions are violet-blue to blue, and on addition of alkali hydroxides deposit the base as a bluish-violet, flocculent precipitate. The base, which forms a blue, metallic powder, melts at 251°, and is moderately soluble in boiling methyl or ethyl alcohol or in acetone, may have the constitution $NMe_2\cdot C_6H_3<^{\;\;N}_{O(OH)}>C_6H(OH)_2\cdot CO\cdot NH_2$, or that of the anhydride, $NMe_2\cdot C_6H_3\left\langle\begin{array}{l} N:C_6H(OH)\cdot CO\cdot NH_2 \\ O-O \end{array}\right.$.

Cœlestine-blue (*p*-diethylaminodihydroxycarbamidophenoxazonium chloride) is formed from nitrosodiethylaniline and gallamide in the same manner as gallamine-blue, but is more soluble. The *dye-base*, $C_{17}H_{17}O_4N_3$ or $C_{17}H_{19}O_5N_3$, resembles that of gallamine-blue. Diethylaminoazobenzene and gallamide condense in glacial acetic acid solution at 110—120°. The *dye-base*, which has the constitution of the base of cœlestine-blue, separates from the alkaline solution as a blue, flocculent precipitate, crystallises from benzene in microscopic leaflets, and melts under boiling water.

The leuco-derivatives of the gallocyanin dyes are obtained as the stannous chloride or the zinc chloride double salt by reduction with stannous chloride or zinc and hydrochloric acid. These leuco-derivatives are unstable with the exception of the derivatives of prune.

Leuco-prune hydrochloride is formed best by the action of concentrated hydrochloric acid on leuco-diacetylprune. Leuco-prune zinc chloride, $C_{16}H_{16}O_5N_2Cl,ZnCl_2$, crystallises from glacial acetic acid in greenish-yellow needles, melts and decomposes at 268°, dissolves in water to form a solution which changes through brown to violet-red, and finally to violet-blue, and in concentrated hydrochloric acid forms a brown, or in concentrated sulphuric acid a violet, solution, which on dilution with water becomes red.

The *benzenesulphonyl* ester of gallamine-blue,

$$NMe_2,C_6H_3<^{N}_{O}>C_6HO(CO\cdot NH_2)\cdot O\cdot SO_2Ph,$$

formed by the action of benzenesulphonyl chloride on the dye dissolved in aqueous sodium carbonate, crystallises from aniline in long, glistening needles, or from a mixture of nitrobenzene, alcohol, and ether in glistening, green, microscopic leaflets, decomposes at 230—240°, and is moderately soluble in boiling acetone, xylene, or methyl, ethyl, or amyl alcohol, forming solutions which are violet-blue by transmitted, carmine-red by reflected, light.

The *benzenesulphonyl* ester of cœlestine-blue, $C_{23}H_{21}O_6N_3S$, crystallises in green, glistening leaflets. The *benzenesulphonyl* ester of prune, $NMe_2\cdot C_6H_3\left\langle\begin{array}{l} N:C_6H(CO_2Me)\cdot O\cdot SO_2Ph \\ O-O \end{array}\right.$, is obtained as a green powder,

which forms in boiling aqueous sodium hydroxide a brown, in hydrochloric acid a red, and in sulphuric acid a bluish-violet, solution. The o-*toluenesulphonyl* ester of prune, $C_{23}H_{20}O_7N_2S$, crystallises from hot nitrobenzene in dark green, glistening leaflets. The p-*toluenesulphonyl* ester of prune crystallises in flat, green, microscopic needles, and when boiled with acetic anhydride in a reflux apparatus yields the *diacetyl* derivative, $C_{27}H_{26}O_9N_2S$, which crystallises in yellow needles, melts at 245°, and dissolves in concentrated sulphuric acid to form a bluish-green solution.

When heated with sodium acetate, acetic anhydride, and glacial acetic acid at 100°, and finally at 150°, prune forms a *triacetyl* derivative, $NMe_2\cdot C_6H_3<\genfrac{}{}{0pt}{}{NAc}{-O-}>C_6H(OAc)_2\cdot CO_2Me$, or

$$NMe_2\cdot C_6H_3<\genfrac{}{}{0pt}{}{-N-}{OAc}\geqslant C_6H(OAc)_2\cdot CO_2Me,$$

or $NMe_2\cdot C_6H_4\cdot NH\cdot C_6H(OAc)_3\cdot CO_2Me$, which crystallises in lemon-yellow needles, sinters at 219°, and melts at 225°. It dissolves in concentrated sulphuric acid to form an emerald-green or blue solution, which becomes red on addition of water, and when treated with ammonia deposits the leuco-base as an apple-green, flocculent precipitate (compare Nietzki and Otto, Abstr., 1888, 949; Möhlau and Klimmer, *Zeit. Farb. Textilchem.*, 1902, i, 65; Henrich and Schierenberg, Abstr., 1904, i, 1049).

When boiled with acetic anhydride in a reflux apparatus, the *o*-toluenesulphonyl ester of prune forms a *diacetyl* derivative, $C_{27}H_{25}O_9N_2S$, which crystallises from ethyl acetate in yellowish-green needles and melts at 201—202°. The *product* obtained on boiling the benzenesulphonyl ester of prune with acetic anhydride and sodium acetate crystallises from ethyl acetate in small, yellow needles, sinters at 116°, and melts at 121°.

When reduced with stannous chloride and acetic anhydride in presence of sodium acetate, prune forms *diacetyl-leuco-prune*, $C_{20}H_{20}O_7N_2$, which is formed also by heating leuco-prune with acetic anhydride and sodium acetate at 130° in an atmosphere of carbon dioxide. It crystallises from toluene in orange needles, or from alcohol in long, golden needles, and melts at 168°. When heated with acetic anhydride, stannous chloride, and sodium acetate at 130°, leuco-prune forms a *mixture* of di- and tri-acetyl derivatives, which crystallises in yellow needles and melts at 184·5°.

Acetyl-leuco-prune benzenesulphonate,

$$NMe_2\cdot C_6H_3<\genfrac{}{}{0pt}{}{NH}{-O-}>C_6H(OAc)(CO_2Me)\cdot O\cdot SO_2Ph,$$

is formed by shaking the benzenesulphonate with acetic anhydride and stannous chloride and boiling the product with sodium acetate. It crystallises in yellow needles, melts at 146°, and dissolves in concentrated sulphuric acid, forming a blue solution which becomes red on dilution. *Acetyl-leuco-prune* o-*toluenesulphonate*,

$$NMe_2\cdot C_6H_3<\genfrac{}{}{0pt}{}{NH}{-O-}>C_6H(OAc)(CO_2Me)\cdot O\cdot SO_2\cdot C_7H_7,$$

formed in the same manner as the acetylbenzenesulphonate, crystal-

lises in orange needles, which appear violet-blue by transmitted light, and melts at 211°.

Acetyl-leuco-prune p-*toluenesulphonate* crystallises from alcohol in short, yellow needles and melts at about 169°. Leuco-prune hydrochloride is obtained on hydrolysis of the diacetyl, but not of the triacetyl, derivative with hydrochloric acid. G. Y.

Piperazine Derivatives from Methylchloroethylamine and Chloroethylpiperidine. LUDWIG KNORR, H. HÖRLEIN, and PAUL ROTH (*Ber.*, 1905, 38, 3136—3141. Compare this vol., i, 1; Knorr, Abstr., 1904, i, 938; Marckwald and Frobenius, Abstr., 1902, i, 22).—Marckwald and Frobenius' polymeric base, $C_6H_{14}N_2$, formed along with *n*-methylethylenimine by the action of sodium hydroxide on methylchloroethylamine hydrochloride, is shown to be 1 : 4-dimethylpiperazine. It boils at 131—132° under 750 mm. pressure; the picrate decomposes at 280°; the aurichloride decomposes at 220°; the platinichloride decomposes at 270°.

Marckwald and Frobenius' supposed ethylenepiperidinium chloride, obtained by boiling 1-chloroethylpiperidine, is diethylenedipiperidinium chloride, $CH_2{<}{CH_2 \cdot CH_2 \atop CH_2 \cdot CH_2}{>}NCl{<}{CH_2 \cdot CH_2 \atop CH_2 \cdot CH_2}{>}NCl{<}{CH_2 \cdot CH_2 \atop CH_2 \cdot CH_2}{>}CH_2$. The picrate, $C_{26}H_{32}O_{14}N_8$, crystallises from boiling water in glistening, rhombic, dichroic leaflets and decomposes at about 300°. When distilled with 50 per cent. aqueous potassium hydroxide, the chloride yields acetylene, ethylenedipiperidine, and 1-hydroxyethylpiperidine. Ethylenedipiperidine, $C_{12}H_{24}N_2$ (Brühl, *Ber.*, 1874, 4, 738), boils at 263° under 745 mm. pressure and is easily soluble in alcohol or ether. The *picrate*, $C_{12}H_{24}N_2,2C_6H_3O_7N_3$, crystallises in long, rhombic needles, decomposes at 225°, and is soluble in 250 parts of boiling, or in 2300 parts of water at 15°. The aurichloride forms prismatic crystals and decomposes at about 207°; the platinichloride, $C_{12}H_{24}N_2,H_2PtCl_6$, crystallises in glistening, monoclinic leaflets and decomposes at 255°. The base reacts with ethylene dibromide to form a quaternary salt, which on conversion into the corresponding chloride is found to be identical with diethylenedipiperidinium chloride formed from 1-chloroethylpiperidine. Contrary to Marckwald and Frobenius's statement, the chloride remains unchanged when heated with concentrated hydrochloric acid at 100° for two hours.

G. Y.

Constitution of Histidine. F. KNOOP and ADOLF WINDAUS (*Beitr. chem. Physiol. Path.*, 1905, 7, 144—147).—*Glyoxaline*-4-*propionic acid*, ${NH \cdot CH \atop CH{=\!=}N}{\gg}C \cdot CH_2 \cdot CH_2 \cdot CO_2H$, may be synthesised by the action of formaldehyde and ammonia on Wolff's glyoxylpropionic acid (Abstr., 1891, 416). It crystallises from dilute acetone in rectangular plates, decomposes at 208—209°, is readily soluble in water, less readily in alcohol, and is insoluble in ether or acetone. The *phosphotungstate* decomposes at a temperature above 300°; the *nitrate* crystallises in six-sided plates, is insoluble in ether, and decomposes at 143—148°; the *platinichloride* crystallises in yellowish-red cubes somewhat readily soluble in hot water, and melts and decomposes at

209°. The *hydrochloride* and *hydriodide* are readily soluble and the *mercuric* and *silver* salts insoluble. The *copper* salt crystallises from hot water in small blue needles The same acid may be obtained by the reduction of Fränkel's hydroxydiaminohistidine (Abstr., 1903, i, 650) with red phosphorus and concentrated hydriodic acid at 150°. This method of formation is an additional argument in favour of Pauly's conclusion that histidine is an α-amino-β-glyoxaline-4-propionic acid (Pauly, Abstr., 1904, i, 1068). J. J. S.

Compound of Pyramidone with Mercuric Chloride. CHARLES ASTRE and G. BÉCAMEL (*Bull. Soc. chim.*, 1905, [iii], **33**, 1084—1087). —When a solution of mercuric and sodium chlorides in water is added to a solution of pyramidone in water, a precipitate of an additive *compound* of pyramidone (1 mol.) with mercuric chloride (1 mol.) is formed. This melts at 157—158° and is soluble in alcohol, ether, or acetone. Its reactions with a number of reagents are given in the original. When the precipitation takes place in presence of hydrochloric acid, the *hydrochloride* of the additive compound separates. It melts at 197—198° and is slightly soluble in alcohol or ether, more so in acetone or water. These substances appear to be similar in constitution to the antipyrine compounds described by Schuyten (Abstr., 1898, i, 452) and unlike those obtained by Ville and Astre (Abstr., 1900, i, 362, 411). T. A. H.

Pyrimidines: 5-Amino-6-oxy-2-ethylthiolpyrimidine. XI. TREAT B. JOHNSON (*Amer. Chem. J.*, 1905, **34**, 191—204).—By the condensation of ethyl formate with ethyl carbethoxyaminoacetate in presence of sodium, the *sodium* derivative of ethyl formylcarbethoxyaminoacetate is produced, which, when added to an aqueous solution of ψ-ethylthiocarbamide, yields trans-*α-carbethoxyamino-β-ψ-ethylthiocarbamideacrylic acid*, $CO_2Et\cdot NH\cdot C(CO_2H)\colon CH\cdot N\colon C(SEt)\cdot NH_2$, which crystallises from hot water in colourless, microscopic prisms and decomposes at 259°; a yield of 40—46 per cent. of the theoretical was obtained. When this compound is dissolved in warm acetic anhydride, it is converted into *5-carbethoxyamino-6-oxy-2-ethylthiolpyrimidine*, $NH<\begin{matrix}C(SEt)=\!=\!=\!=\!=N\\CO\cdot C(NH\cdot CO_2Et)\end{matrix}>CH$, which crystallises in prisms and melts at 189—190°. If either the acid or the pyrimidine just described is boiled with solution of sodium hydroxide, *5-amino-6-oxy-2-ethylthiolpyrimidine*, $NH<\begin{matrix}C(SEt)=N\\CO\cdot C(NH_2)\end{matrix}>CH$, is obtained, which crystallises from hot water in groups of radiating needles and melts at 160°. When the *trans*-acid is boiled with dilute sodium hydroxide and the product, after being acidified with nitric acid, is treated with solution of silver nitrate, the *di-silver* salt of *5-carboxylamino-6-hydroxy-2-ethylthiolpyrimidine*, $N\leqslant\begin{matrix}C(SEt)=\!=\!=\!=\!=\!=\!=N\\C(OAg)\cdot C(NH\cdot CO_2Ag)\end{matrix}\geqslant CH$, is produced as an amorphous precipitate.

6-Chloro-5-phosphoryldichloroamino-2-ethylthiolpyrimidine,

$$N\leqslant\begin{matrix}C(SEt)=\!=\!=\!=\!=N\\CCl\cdot C(NH\cdot POCl_2)\end{matrix}\geqslant CH,$$

obtained by the action of phosphorus oxychloride on 5-amino-6-oxy-2-ethylthiolpyrimidine, is a yellow, crystalline substance which decomposes at about 247—250°. When this compound is heated with alcoholic ammonia at 160—165° for three hours, *6-chloro-5-phosphoryltriamino-2 ethylthiolpyrimidine*, $N\ll\begin{matrix}C(SEt)=\!=\!=\!=\!=N\\ CCl\cdot C[NH\cdot PO(NH_2)_2]\end{matrix}\gg CH$, is formed, which has a green, metallic appearance, sinters at about 258°, decomposes at 290—300°, and is insoluble in water or the usual organic solvents.

When 5-benzoylamino-2-ethylthiol-6-oxypyrimidine (Johnson and Clapp, Abstr., 1904, i, 820) is boiled with solution of sodium hydroxide, the *sodium* salt of *α-benzoylamino-β-ψ-ethylthiolcarbamideacrylic acid*,

$$NH_2\cdot C(SEt)\colon N\cdot CH\colon C(NHBz)\cdot CO_2Na,$$

is obtained, which crystallises in needles, melts and decomposes at 124—125°, and is reconverted by acids into the pyrimidine.

5-Benzylideneamino-6-oxy-2-ethylthiolpyrimidine,

$$NH<\begin{matrix}C(SEt)=\!=\!=\!=N\\ CO\cdot C(N\colon CHPh)\end{matrix}>CH,$$

prepared by the action of benzaldehyde on 5-amino-6-oxy-2-ethylthiolpyrimidine, crystallises from benzene in plates or prisms and melts at 185—187°.

5-Benzoylamino-2-thion-6-oxypyrimidine, $NH<\begin{matrix}CS\text{———}NH\\ CO\cdot C(NHBz)\end{matrix}>CH$, obtained by the action of thiocarbamide on the sodium derivative of ethyl hydroxymethylenehippurate, crystallises in plates, decomposes at 300—310°, and is insoluble in water or alcohol.

[By S. H. Clapp.]—By the action of phosphorus oxychloride on 5-benzoylamino-2-ethylthiol-6-oxypyrimidine, *2-ethylthiol-5 : 6-μ-phenyloxazolinepyrimidine*, $SEt\cdot C\ll\begin{matrix}N=\!=\!=C\cdot O\\ N\cdot CH\colon \overset{|}{C}\cdot N\end{matrix}\gg CPh$, is produced as a white, crystalline solid, which melts at 108—109° and is reconverted by hydrochloric acid into the original pyrimidine; the *hydrochloride* melts and decomposes at 147°. E. G.

Pyrimidines: Action of Aqueous and Alcoholic Ammonia and Aniline on some Halogen- and Thiol-pyrimidines. X. Treat B. Johnson and Karl O. Johns (*Amer. Chem. J.*, 1905, **34**, 175—191).—*6-Amino-4-oxy-2-methylthiolpyrimidine*,

$$N\ll\begin{matrix}C(SMe)=\!=N\\ C(NH_2)\cdot CH_2\end{matrix}>CO,$$

obtained by the action of methyl iodide (1 mol.) on 6-amino-4-oxy-2-thiopyrimidine (Traube, Abstr., 1904, i, 632) in presence of sodium ethoxide (1 mol.), crystallises from hot alcohol in colourless plates and decomposes at 267°. If 2 mols. of methyl iodide and sodium ethoxide are used, *4-methoxy-6-amino-2-methylthiolpyrimidine*,

$$N\ll\begin{matrix}C(SMe)=N\\ C(NH_2)\cdot CH\end{matrix}\gg C\cdot OMe,$$

is produced, which crystallises from alcohol in long prisms and melts and decomposes at 256°. *5-Bromo-6-amino-4-oxy-2-methylthiolpyrimidine*, $N\ll\begin{matrix}C(SMe)=\!=\!=N\\ C(NH_2)\text{—}CHBr\end{matrix}>CO$, crystallises in slender prisms, becomes

brown above 200°, and does not melt below 300°. 6-*Amino*-4-*oxy*-2-*ethylthiolpyrimidine*, $N{<}\begin{matrix}C(SEt)=\!=\!=N\\C(NH_2)-CH_2\end{matrix}{>}CO$, prepared in the same manner as the corresponding methyl derivative, crystallises from water in long, slender prisms, is very soluble in alcohol, and melts at 216—217°.

4-Chloro-6-amino-2-methylthiolpyrimidine, which was first obtained by Wheeler and Jamieson (Abstr., 1904, i, 940) by heating 4 : 6-dichloro-2-methylthiolpyrimidine with alcoholic ammonia, can be prepared more easily by the action of phosphorus oxychloride on 6-amino-4-oxy-2-methylthiolpyrimidine. When this chloro-compound is heated with concentrated aqueous ammonia at 185—195° for five hours, 4 : 6-diamino-2-methylthiolpyrimidine (Wheeler and Jamieson, *loc. cit.*) is formed, which is very stable and can be heated with a concentrated solution of ammonia, either aqueous or alcoholic, at 205—215° without change. 4-*Chloro*-5-*bromo*-6-*amino*-2-*methylthiolpyrimidine*,

$$N{<}\begin{matrix}C(SMe)=\!=\!=N\\C(NH_2)-CBr\end{matrix}{>}CCl,$$

obtained by the action of bromine on 4-chloro-6-amino-2-methylthiolpyrimidine, melts at 165° and is sparingly soluble in water; its *hydrobromide* melts at 180—190° and decomposes at 208°. When this compound is heated with aqueous ammonia for four hours at 150—160°, 5-*bromo*-4 : 6-*diamino*-2-*methylthiolpyrimidine*,

$$N{<}\begin{matrix}C(SMe)=\!=\!=N\\C(NH_2)-CBr\end{matrix}{>}C{\cdot}NH_2,$$

is produced, which crystallises from hot water in large prisms and melts at 192°. This substance is not obtained if alcoholic ammonia is substituted for the aqueous solution, and it is very stable in contact with either aqueous or alcoholic ammonia at 200—210°.

5-*Bromo*-6-*amino*-2-*thion*-4-*oxypyrimidine*, $N{<}\begin{matrix}CS-\!-\!-\!-NH\\C(NH_2){\cdot}CHBr\end{matrix}{>}CO$, obtained by the action of bromine on 6-amino-2-thion-4-oxypyrimidine, forms granular crystals, does not melt below 300°, and is sparingly soluble in acetic acid and insoluble in water.

When 4-chloro-6-amino-2-methylthiolpyrimidine is heated with aniline (1 mol.), 6-*amino*-4-*anilino*-2-*methylthiolpyrimidine*,

$$N{<}\begin{matrix}C(SMe)=N\\C(NH_2){\cdot}CH\end{matrix}{>}C{\cdot}NHPh,$$

is produced, which crystallises from benzene in groups of microscopic prisms and melts at 124°; the *dihydrochloride* melts and decomposes at 121°. If 2 mols. of aniline are employed, 6-*amino*-2 : 4-*dianilinopyrimidine*, $N{<}\begin{matrix}C(NHPh){:}N\\C(NH_2){\cdot}CH\end{matrix}{>}C{\cdot}NHPh$, is formed, which melts at 65—70° and is extremely soluble in the ordinary organic solvents; the *sulphate* melts and decomposes at 190—193°. 5-*Bromo*-6-*amino*-4-p-*bromoanilino*-2-*methylthiolpyrimidine*, $N{<}\begin{matrix}C(SMe)=\!=\!=N\\C(NH_2)-CBr\end{matrix}{>}C{\cdot}NH{\cdot}C_6H_4Br$, obtained by the action of bromine on 6-amino-4-anilino-2-methylthiolpyrimidine, crystallises in long, slender prisms and melts at 202°; the *hydrobromide* decomposes at 290°. This compound is also produced when 4-chloro-5-bromo-6-amino-2-methylthiolpyrimidine is heated with *p*-bromoaniline.

4-*Chloro-5-bromo-6-amino-2-oxypyrimidine*, $N\begin{matrix}\diagup CO\text{——}NH\diagdown \\ \diagdown C(NH_2)\cdot CBr\diagup\end{matrix}CCl$, formed by the action of bromine on 4-chloro-6-amino-2-oxypyrimidine, crystallises from hot water in groups of microscopic prisms, becomes brown at 210°, and decomposes at about 230°; the *hydrobromide* decomposes at 230—240°.

6-Chloro-2-ethylthiolpyrimidine is unaffected by aqueous ammonia at 140—150°, but when heated with the reagent at 185—195° is converted into 2 : 6-diaminopyrimidine. When 6-chloro-5-bromo-2-ethylthiolpyrimidine (Wheeler and Johnson, Abstr., 1904, i, 625) is heated with aqueous ammonia at 140—150° or at 185—195°, 5-bromo-6-amino-2-ethylthiolpyrimidine is produced. E. G.

Condensation of Ethyl Acetoacetate with Phenylmethylpyrazolone and the Products formed by the Action of Hydrazine and of Phenylhydrazine on Dehydracetic Acid. ROBERT STOLLÉ (*Ber.*, 1905, **38**, 3023—3032. Compare Knorr, Abstr., 1887, 678).—A condensation product, $C_{16}H_{18}O_3N_2$, of ethyl acetoacetate and phenylmethylpyrazolone is formed when the two substances are mixed, the water formed removed, and the mixture then heated on the water-bath for several hours. It is always accompanied by Knorr's lactone, melting at 145°, and crystallises from alcohol in glistening, yellow needles melting at 98° and readily soluble in ether, alcohol, or benzene. When heated at 150°, it loses alcohol and yields Knorr's lactone. With nitrous acid, it yields an iso*nitroso*-derivative, $C_{16}H_{17}O_4N_3$, which crystallises from alcohol in slender, orange-red needles, melting and decomposing at about 198°. A *silver* derivative, $C_{16}H_{16}O_4N_3Ag,AgNO_3$, has been prepared. When hydrolysed with 2 per cent. aqueous sodium hydroxide, the condensation product yields Knorr's 1-phenyl-3-methyl-4-*iso*propylene-5-pyrazolone. When ethylated, the product yields the *ethoxypyrazolone* derivative, $C_{18}H_{22}O_3N_2$, which crystallises from alcohol in glistening, hard prisms, melting at 117°, and is soluble in organic solvents, but insoluble in alkalis or acids. The reactions of the condensation product agree with either the formula

$$CO_2Et\cdot CH_2\cdot CMe{:}C\begin{matrix}\diagup CMe{:}N \\ \diagdown CO\text{—}NPh\end{matrix}$$

or the tautomeric formula $CO_2Et\cdot CH{:}CMe\cdot CH\begin{matrix}\diagup CMe{:}N \\ \diagdown CO\text{—}NPh\end{matrix}$.

To Knorr's lactone, melting at 145°, is attributed the constitutional formula $\begin{matrix}CH{:}CMe\cdot C\cdot CMe \\ CO\cdot O\text{——}C\cdot NPh\end{matrix}\!\!>\!N$.

Ethyl ethylacetoacetate and phenylmethylpyrazolone, when heated at 160°, yield a *lactone*, $C_{16}H_{16}O_2N_2$, which crystallises in colourless needles melting at 142°.

The phenylhydrazone of dehydracetic acid (Perkin, Trans., 1887, **51**, 494), when heated with ether and acetyl chloride or with alcohol and concentrated hydrochloric acid, yields a *product*,

$$\begin{matrix}CH\cdot CO\cdot C\cdot CMe \\ CMe\text{—}O\cdot C\cdot NPh\end{matrix}\!\!>\!N,$$

isomeric with Knorr's lactone. It crystallises in slender needles,

melts at 158°, and is insoluble in acids and alkalis. Mohr's phenylmethylpyrazylphenylmethylpyrazolone melting at 260° is usually formed as a by-product (this vol., i, 676).

Dehydracetic acid and hydrazine hydrate react, yielding the *hydrazone*, $C_8H_{10}O_3N_2$. This crystallises in slender needles, turns yellow at 150°, melts and decomposes at 208°, dissolves in hot water, dilute acids, and alcohol, and reduces ammoniacal silver nitrate. Its *benzylidene* derivative, $C_{15}H_{14}O_3N_2$, crystallises in yellowish-green needles and melts at 191°.

The *ketazine*, $C_{16}H_{14}O_6N_2$, is formed as a by-product in the preparation of the hydrazone, and is also formed when acid solutions of the latter are heated. It crystallises from acetic acid in yellowish-green needles, melts at 265°, dissolves sparingly in hot alcohol, and is insoluble in water, ether, or dilute acids.

Methylpyrazylmethylpyrazolone, $\begin{array}{l}\text{CMe}\cdot\text{CH}\\ \text{N}\text{——}\text{NH}\end{array}\!\!>\!\text{C}\cdot\text{CH}\!<\!\!\begin{array}{l}\text{CMe:N}\\ \text{CO—NH}\end{array}$, obtained by the action of an excess of hydrazine hydrate on dehydracetic acid, melts at 260°, and is soluble in alcohol and in alkalis. The *silver* salt has been prepared. J. J. S.

Azine of Ethyl Acetoacetate. LUDWIG WOLFF (*Ber.*, 1905, 38, 3036—3041. Compare Abstr., 1904, i, 722, and Stollé, preceding abstract).—*Ethyl* 3-*methylpyrazolone*-4-iso*propylenecarboxylate*,

$$\text{COEt}\cdot\text{CH:CMe}\cdot\text{CH}\!<\!\!\begin{array}{l}\text{CMe:N}\\ \text{CO—NH}\end{array}\ ^*,$$

is formed together with methylpyrazolone by the action of dilute ammonia on ethyl azoacetoacetate, also when the azine is boiled with 50 per cent. alcohol, but most readily by the action of aqueous sodium hydroxide on a mixture of methylpyrazolone and ethyl acetoacetate. It forms minute crystals from alcohol, dissolves in sodium carbonate solution and also in dilute hydrochloric acid, and gives a red coloration with ferric chloride. When rapidly heated, the ester decomposes at about 186°, yielding ethyl alcohol and the lactone,

$$\begin{array}{l}\text{CH:CMe}\cdot\text{C}\cdot\text{CMe}\\ \text{CO}\cdot\text{O}\text{——}\text{C}\cdot\text{NH}\end{array}\!\!>\!\text{N},$$

which corresponds with Knorr's lactone melting at 145°. The same lactone is formed when ethyl azoacetoacetate is heated at 160—180°, or when molecular quantities of methylpyrazolone and ethyl acetoacetate are heated at 160—180° (compare Rosengarten, Abstr., 1894, i, 546). When hydrolysed with cold sodium hydroxide solution, it yields 3-*methylpyrazolone*-4-iso*propylenecarboxylic acid*,

$$\text{CO}_2\text{H}\cdot\text{CH}\cdot\text{CMe:CH}\!<\!\!\begin{array}{l}\text{CMe:N}\\ \text{CO—NH}\end{array}\ ^*;$$

this melts at 145°, dissolves sparingly in water, alcohol, or ether, but readily in sodium carbonate or 10 per cent. hydrochloric acid. An *isomeric acid*, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CMe:C}\!<\!\!\begin{array}{l}\text{CMe:N}\\ \text{CO—NH}\end{array}\ ^*$, melting at 131°, is formed by the action of cold 10 per cent. sodium hydroxide on ethyl

* The position of the double linking in the side chain has not been determined with certainty.

azoacetoacetate. It is somewhat more stable than its isomeride, but both are decomposed into carbon dioxide and 3-*methyl*-4-iso*propylene-pyrazolone*, $C_7H_{10}ON_2$. The same products are formed when the acid melting at 145° is heated with alcohol or water at 60—70°. The pyrazolone derivative crystallises from alcohol in colourless prisms melting at 223—224°. It gives the ferric chloride reaction, and may be synthesised from acetone and methylpyrazolone in sodium carbonate solution.

Methylpyrazolone and acetylacetone yield the *product*,

$$\begin{matrix} N{:}CMe \\ | \\ NH{-}CO \end{matrix}\!\!>C{:}CMe\cdot CH_2\cdot CMe{:}C<\!\!\begin{matrix} CMe{:}N \\ \quad | \\ CO{-}NH \end{matrix},$$

melting at 206°. It is insoluble in alkalis and gives no coloration with ferric chloride. J. J. S.

Dihydroazines. OSCAR HINSBERG (*Ber.*, 1905, **38**, 2800—2803. Compare Hinsberg and Garfunkel, Abstr., 1897, i, 123; Tichwinsky and Wolochowitsch, this vol., i, 383).—Hinsberg and Garfunkel's *s*-diacetyldihydrophenazine is obtained when the monoacetyl compound is boiled for some time with acetic anhydride. It would thus appear that the primary dihydro-derivative has the unsymmetrical structure and yields a monoacetyl derivative, but that on further acetylating molecular rearrangement occurs, and the *s*-diacetyl compound is obtained.

$$C_6H_4\lessgtr{}^{N}_{N}\!>C_6H_4 \longrightarrow C_6H_5\lessgtr{}^{NH}_{N-}\!>C_6H_4$$

$$\longrightarrow C_6H_5\lessgtr{}^{NAc}_{N—}\!>C_6H_4 \longrightarrow C_6H_4<{}^{NAc}_{NAc}\!>C_6H_4.$$

This is used in support of the view of the quinonoid structure of phenazine and similar compounds (compare Abstr., 1902, i, 238). J. J. S.

Dihydrophenazine. WLADIMIR G. SCHAPOSCHNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 567—568).—The author objects to the unsymmetrical structure for phenazine given by Tichwinsky and Wolochowitsch (this vol., i, 383), the results obtained by the latter giving no definite indications on this head. Further, scarcely any analogy exists between the properties of the indulines and safranines and those of phenazine, the known properties of which do not support a quinonoid structure. The symmetrical formula for phenazine gives a much better explanation of the work of Wohl and Aue (Abstr., 1901, i, 612), and of Wohl (Abstr., 1904, i, 155), than the unsymmetrical one. T. H. P.

Trihydroxyphenylrosinduline. KALLE & Co. (D.R.-P. 158101).—The preparation of trihydroxyphenylrosinduline (this vol., i, 554) may be modified by boiling the *p*-aminophenol and the naphthalene base together in aqueous solution or suspension in a reflux apparatus for 5—6 hours. A purer product is obtained than when fusion is employed. C. H. D.

Unsymmetrical Safranines. PHILIPPE BARBIER and PAUL SISLEY (*Bull. Soc. chim.*, 1905, [iii], **33**, 995—998. Compare Barbier and Vignon, Abstr., 1888, 54, 141, 688).—Safranines are generally represented as having symmetrical constitutions, which, however,

does not agree always with their properties. That unsymmetrical safranines may exist is shown by the formation of phenosafranine by the oxidation of a mixture of 2 : 4′-diaminodiphenylamine and aniline hydrochlorides by potassium dichromate in neutral solution. It must have the unsymmetrical formula

$$C_6H_4{<}\begin{array}{l}N{=\!=\!=\!=\!=\!=}C{\cdot}CH{:}CH \\ N(C_6H_4{\cdot}NH_2){\cdot}C{:}CH{\cdot}C{:}NH\end{array}$$

as the similar oxidation of a mixture of 2 : 4 : 4′-triaminodiphenylamine and aniline hydrochlorides leads to the formation of Ris' aminophenosafranine, $\begin{array}{l}CH{:}CH{-\!-}C{\cdot}N{=\!=\!=\!=\!=}C{\cdot}CH{:}CH \\ C(NH_2){:}CH{\cdot}C{\cdot}N(C_6H_4{\cdot}NH_2){\cdot}C{:}CH{\cdot}C{:}NH\end{array}$ (Abstr., 1895, i, 148). The amino-group introduced by the aniline must assume, therefore, the *para*-position. G. Y.

Condensation of Ethyl Succinylsuccinate with Guanidine. Derivative of 1:3:6:8-Naphthatetrazine, a New Heterocycloid. MARSTON T. BOGERT and ARTHUR WAYLAND DOX (*J. Amer. Chem. Soc.*, 1905, **27**, 1127—1140).—Ethyl *p*-diaminoterephthalate was prepared by Baeyer's method (Abstr., 1886, i, 445), which consists in converting ethyl succinylsuccinate into the di-imine, and oxidising the latter with bromine. The di-imine melts at 177—178°, and not at 181°, as stated by Baeyer. When the ester was treated with acetic anhydride, it dissolved, but no acetyl derivative could be isolated. The ester reacts with phenylcarbimide and with phenylthiocarbimide to form compounds which in general behaviour resemble the naphthatetrazine derivative described later. The product obtained with phenylthiocarbimide is yellow and very sparingly soluble in water or alcohol, but dissolves more readily in phenol, aniline, pyridine, or quinoline to form solutions with a yellowish-green fluorescence.

Ethyl succinylsuccinate does not react with carbamide or with phenylcarbimide. When the ester is heated with an alcoholic solution of guanidine thiocyanate or acetate in presence of sodium ethoxide, a yellowish-white precipitate is produced which is insoluble in water and most organic solvents, but is slightly soluble in alcohol. This *compound* is a derivative of 1 : 3 : 6 : 8-naphthatetrazine, and has the formula

$$\begin{array}{l}\quad\; N{\cdot}CO{\cdot}CH{\cdot}CH_2{\cdot}C{=\!=}N{\cdot}C{\cdot}NH_2 \\ NH_2{\cdot}C{-}N{:}C{-}CH_2{\cdot}CH{\cdot}CO{\cdot}N\end{array} \quad \text{or}$$

$$\begin{array}{l}\quad\; NH{:}CO{\cdot}CH{\cdot}CH_2{\cdot}C{=\!=}N{\cdot}C{:}NH \\ NH{:}C{-\!-}N{:}C{\cdot}CH_2{-}CH{\cdot}CO{\cdot}NH\end{array}.$$

When heated, it does not melt, but ammonia is evolved, and the mass becomes charred. The *hydrochloride* and *sulphate* are described. The *sodium* derivative crystallises with $6H_2O$, and is strongly fluorescent; the *potassium* derivative was also prepared. E. G.

The Pyrrole-blue Group. CARL LIEBERMANN and G. HÄSE (*Ber.*, 1905, **38**, 2847—2853. Compare Liebermann and Mauthner, Abstr., 1904, i, 684; Ciamician and Silber, Abstr., 1884, 740; Meyer and Stadler, *ibid.*, 1045).—Pyrrole-blue A, $C_{24}H_{18}O_3N_4$, is obtained as a blue precipitate when 5 grams of freshly distilled pyrrole are added to 10 grams of isatin dissolved in 5½ litres of water con-

taining 50 grams of concentrated sulphuric acid, and cooled to 5° with ice. The dry powder has an indigo-blue colour, cannot be purified by recrystallisation, and dissolves in concentrated sulphuric acid to form a violet solution which becomes bluish-black. When dissolved in pyridine and boiled with acetic anhydride, it yields only 6—12 per cent. of a derivative which is probably *acetylpyrrole-blue* B, $C_{24}H_{16}O_2N_4Ac_2$, derived from a small quantity of pyrrole-blue B present in the precipitate. It forms glistening, golden, microscopic needles, is soluble in hot pyridine or hot glacial acetic acid forming blue solutions, and dissolves in cold concentrated sulphuric acid to form a rosaniline-red solution which becomes blue; on immediate addition of water, the sulphuric acid solution deposits the unchanged acetyl derivative, but after the colour-change has taken place the precipitate consists of *acetylpyrrole-blue*-B-*disulphonic acid*, $C_{28}H_{20}O_4N_4(SO_3H)_2$. On evaporation of its blue, aqueous solution, this is obtained as a copper-coloured filament on the glass walls of the vessel. It dyes silk blue in aqueous solution, and forms a *barium* salt, $C_{28}H_{20}O_4N_4(SO_3)_2Ba$, on addition of barium chloride to its slightly ammoniacal solution. On warming the original sulphuric acid solution on the water-bath, a higher *sulphonic acid*, which is red and more easily soluble, is formed.

Pyrrole-blue B, $C_{24}H_{18}O_2N_4$, is formed when a solution of 0·75 gram of pyrrole in 10 c.c. of glacial acetic acid is added to a mixture of 100 c.c. of a 1 per cent. solution of isatin in glacial acetic acid and 40 c.c. of 15 per cent. sulphuric acid, cooled to 0° by ice-water; after five minutes, 10 c.c. of ice-water are added and the product filtered. After boiling the dried precipitate 3 to 4 times with pyridine, it is obtained as a glistening powder resembling cantharidin; it is less soluble than the A-blue, forms blue solutions in boiling glacial acetic acid or pyrrole, and, with concentrated sulphuric acid, gives a violet-red coloration which becomes blue, and on addition of water deposits *pyrrole-blue*-B-*disulphonic acid*, $C_{24}H_{16}O_2N_4(SO_3H)_2$.

Bromo-, dibromo-, and nitro-isatins form metallic, blue derivatives with pyrrole more easily than does isatin.

Tetrabromopyrrole-blue, $C_{24}H_{14}O_2N_4Br_4$, formed from dibromoisatin, is only sparingly soluble and reacts slowly with concentrated sulphuric acid.

1-Ethylpyrrole, 1-acetylpyrrole, indole, furfuraldehyde, and pyromucic acid do not form blue derivatives with isatin.

Schotten's isatin-blue from dipiperidylisatin (Abstr., 1891, 928, 1491) is not identical with Meyer's pyrrole-blue, as it gives a yellowish-brown coloration with concentrated sulphuric acid.

G. Y.

Reduction of Hydroxyazo-compounds to Aminophenols by Phenylhydrazine. GIUSEPPE ODDO and ERNESTO PUXEDDU (*Ber.*, 1905, **38**, 2752—2755).—The reduction of hydroxyazo-compounds to aminophenols by means of phenylhydrazine proceeds in accordance with the scheme $OH{\cdot}R{\cdot}N{:}NPh + 2NHPh{\cdot}NH_2 = OH{\cdot}R{\cdot}NH_2 + H_2NPh + 2C_6H_6 + 2N_2$, where R represents an aromatic group.

When benzeneazo-eugenol is heated with phenylhydrazine at 110—200°, 5-amino-eugenol, melting at 110°, is formed. Similarly,

benzeneazo-*p*-cresol was reduced to the corresponding aminocresol, benzeneazocarvacrol to aminocarvacrol, and benzeneazophenol to *p*-aminophenol. A. McK.

Velocity of Decomposition of *p*-Nitrobenzenediazonium Chloride. Reply to Cain. Carl Schwalbe (*Ber.*, 1905, 38, 3071—3076. Compare this vol., i, 618, and Cain, *ibid.*, 724).—Further experiments confirm the view that the stability of the diazonium salt is decreased by the presence of free nitrous acid, by a high degree of concentration, by absence of mineral acids, and by the action of light. On the other hand, the stability is increased by excess of mineral acids or of mineral salts.

Full details of the method of titration of diazonium salts with β-naphthol are given. J. J. S.

Reducing Action of Organo-magnesium Compounds. Hartwig Franzen and W. Deibel (*Ber.*, 1905, 38, 2716—2718).—Hydrazobenzene is formed by the action of magnesium ethyl bromide on azobenzene, thus: $NPh{:}NPh + 2MgEtBr = MgBr{\cdot}NPh{\cdot}NPh{\cdot}MgBr + C_4H_{10}$ and $MgBr{\cdot}NPh{\cdot}NPh{\cdot}MgBr + 2H_2O = NHPh{\cdot}NHPh + 2MgBr{\cdot}OH$. *p*-Azotoluene is reduced to *p*-hydrazotoluene in a similar manner. Benzylbenzylidenehydrazine is formed in similar manner from magnesium phenylbromide and benzaldazine; it was identified by means of its hydrochloride. A. McK.

Nitro-derivatives of Orange IV. I and II. Paul Juillard (*Bull. Soc. chim.*, 1905, [iii], 33, 974—987, 987—994).—The dyes obtained by nitration of orange IV (anilinobenzeneazobenzene-*p*-sulphonic acid) may be divided into two classes: those, such as Indian yellow 15 and curcumine, which give orange to golden-yellow colours; and those, such as Indian yellow 25 and citronine, which dye wool and silk lemon-yellow shades. The dyes of the former group consist of mixtures of salts of three mononitro-derivatives of orange IV, along with *op'*- and *pp'*-dinitrodiphenylamines; those of the latter group contain salts of dinitro- and trinitro-derivatives of orange IV, along with dinitro-, trinitro-, and sometimes a little tetranitro-diphenylamines. The shade of yellow is influenced by the number of nitro-groups introduced into orange IV, but not by the positions which they assume. Only those nitro-derivatives which are soluble in water are of value as dyes. When orange IV is treated with 1·5 mols. of nitric acid in cold glacial acetic acid solution, the principal product is p-*nitroanilinobenzeneazobenzenesulphonic acid*,

$$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}SO_3H.$$

This is purified by successive treatment with cold glacial acetic acid and warm toluene, and finally by conversion into the *ammonium* or *potassium* salt. These crystallise from dilute ammonium or potassium chloride solutions in yellow needles, and yield the acid when treated with dilute hydrochloric acid. The *sodium* salt, $C_{18}H_{14}O_5N_4SNa,2H_2O$, crystallises in yellow needles and is moderately soluble in cold water. The acid forms a black, crystalline crust and is insoluble in cold water, but dissolves in boiling water to form a yellow solution which, on

addition of hydrochloric or sulphuric acid, gives a bluish-black solution and precipitate. With sodium nitrite, the acid forms a pale yellow *nitrosoamine* which is only sparingly soluble, and on nitration in the cold yields dinitrodiphenylnitrosoamine. With nitric acid in acetic acid solution, the potassium salt forms *p*-nitroanilino-*o*-nitrobenzeneazobenzenesulphonic acid and *pp'*-dinitrodiphenylamine.

o-*Nitroanilinobenzeneazobenzenesulphonic acid,*

$$NO_2\cdot C_6H_4\cdot NH\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot SO_3H,$$

and 4-*anilino*-3-*nitrobenzeneazobenzenesulphonic acid,*

$$C_6H_5\cdot NH\cdot C\lessdot\begin{matrix}CH\text{——}CH\\ C(NO_2)\!:\!CH\end{matrix}\gtrdot C\cdot N_2\cdot C_6H_4\cdot SO_3H,$$

are obtained together by nitration of orange IV with 1 mol. of nitric acid in glacial acetic acid solution at 10—20°. The product is filtered and the filtrate treated with potassium chloride, which precipitates the *potassium* salts of the two *o*-nitro-acids along with a small quantity of dinitrodiphenylamines, which are removed by digestion with toluene. The potassium salts, which form isomorphic, rhombohedral crystals, can be separated by fractional crystallisation from dilute alcohol. The anilino-*o*-nitro-acid is very soluble in water, from its solution in which it is precipitated on adding hydrochloric or sulphuric acid as a brilliant yellow mass, and on treatment with nitric acid yields *p*-nitroanilino-*o*-nitrobenzeneazobenzenesulphonic acid. The *o*-nitroanilino-acid is less soluble in water, yields on addition of hydrochloric or sulphuric acid to its aqueous solution a black precipitate, which redissolves to form a violet solution in excess of acid, and on nitration forms *o*-nitroanilino-*o*-nitrobenzeneazobenzenesulphonic acid, *op'*-dinitrodiphenylamine, and diazobenzenesulphonic acid.

When nitrated in acetic acid solution, the nitroso-derivative of orange IV yields nitroso-4 : 8-dinitro- and nitroso-2 : 8-dinitro-orange IV along with *op'*- and *pp'*-dinitrodiphenylamines. After removal of the latter with excess of nitric acid and elimination of the nitroso-groups from the nitrosodinitro-acids by treatment with alcoholic sulphuric acid, the dinitro-acids are converted into their potassium salts, which are separated by fractional crystallisation. The two dinitro-acids are formed along with *op'*- and *pp'*-dinitrodiphenylamines and diazobenzenesulphonic acid by treatment of orange IV with 2 mols. of nitric acid in acetic or aqueous solution.

4 : 8-*Dinitro-orange* IV (4-p-*nitroanilino*-3-*nitrobenzeneazobenzenesulphonic acid*), $NO_2\cdot C_6H_4\cdot NH\cdot C\lessdot\begin{matrix}CH\text{——}CH\\ C(NO_2)\!:\!CH\end{matrix}\gtrdot C\cdot N_2\cdot C_6H_4\cdot SO_3H$, crystallises in slender, microscopic, yellow needles on addition of sulphuric acid to the aqueous solution of its potassium salt, $C_{18}H_{12}O_7N_5SK,H_2O$. This crystallises in scarlet rhombohedra, is easily soluble in boiling, but only slightly so in cold water, and on nitration in acetic acid solution yields 2 : 4 : 8-trinitro-orange IV and *opp'*-trinitrodiphenylamine. The *sodium* salt, $C_{18}H_{12}O_7N_5SNa,H_2O$, crystallises in small, orange, prismatic needles.

2 : 8-*Dinitro-orange* IV (4-o-*nitroanilino*-3-*nitrobenzeneazobenzenesulphonic acid*),

$$CH\lessdot\begin{matrix}CH\text{——}CH\\ CH\!:\!C(NO_2)\end{matrix}\gtrdot C\cdot NH\cdot C\lessdot\begin{matrix}CH\text{——}CH\\ C(NO_2)\!:\!CH\end{matrix}\gtrdot C\cdot N_2\cdot C_6H_4\cdot SO_3H,$$

crystallises in orange needles, is easily soluble in water, and forms a *potassium* salt, $C_{18}H_{12}O_7N_5SK,2H_2O$, which crystallises in red flakes and is moderately soluble in boiling water; the sodium salt, $C_{18}H_{12}O_7N_5SNa,3H_2O$, crystallises in long, thin, glistening plates. On nitration, 2 : 8-dinitro-orange IV and its salts form 2 : 4 : 8-trinitro-orange IV and *opp'*-trinitrodiphenylamine.

2 : 4-*Dinitro-orange* IV (op-*dinitroanilinobenzeneazobenzenesulphonic acid*), $C_6H_3(NO_2)_2\cdot NH\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot SO_3H,H_2O$, is formed by heating *op'*-dinitrobromobenzene with sodium aminobenzeneazobenzene-*p*-sulphonate in presence of sodium acetate. It separates in orange crystals on addition of sulphuric acid to the solution of its *sodium* salt. This ($3H_2O$) crystallises in orange-red prisms; the *potassium* salt (H_2O) crystallises in stellate groups of dark red prisms and is easily decomposed by carbon dioxide; the *barium* salt,

$$(C_{18}H_{12}O_7N_5S)_2Ba,7H_2O,$$

crystallises in orange needles. When evaporated with hydrochloric acid, these salts are hydrolysed into aminobenzeneazobenzenesulphonic acid and *op*-dinitrophenol. On nitration, the acid and its salts yield *opp'*-trinitrodiphenylamine and 2 : 4 : 8-trinitro-orange IV.

2 : 4 : 8-*Trinitro-orange* IV (4-op-*dinitroanilino-3-benzeneazobenzenesulphonic acid*),

$$NO_2\cdot C{<}{\begin{matrix}CH\text{——}CH\\CH{:}C(NO_2)\end{matrix}}{>}C\cdot NH\cdot C{<}{\begin{matrix}CH\text{——}CH\\C(NO_2){:}CH\end{matrix}}{>}C\cdot N_2\cdot C_6H_4\cdot SO_3H,2H_2O,$$

formed along with *opp'*-trinitrodiphenylamine melting at 188—189°, and *oo'p*-trinitrodiphenylamine melting at 184°, by nitration of orange IV or one of its dinitro-derivatives, crystallises in orange scales and is only slightly soluble in water. The potassium salt ($2H_2O$), crystallises in microscopic flakes and on drying forms a brilliant, dark greenish-brown mass.

2 : 4 : 6-*Trinitro-orange* IV (oop-*trinitroanilinobenzeneazobenzenesulphonic acid*), $C_6H_2(NO_2)_3\cdot NH\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot SO_3H$, is formed by the action of picryl chloride on sodium aminobenzeneazobenzene-*p*-sulphonate in presence of sodium acetate. It is purified by recrystallisation of its *sodium* salt (H_2O), and when warmed with water decomposes into picric and aminobenzeneazobenzenesulphonic acids. The *potassium* salt (H_2O) crystallises in yellow flakes, and, when treated with nitric acid in cold acetic acid solution, yields a substance forming red crystals and picryl-*p*-nitroaniline. This, if the reaction is prolonged, is further nitrated to pentanitrodiphenylamine melting at 193°. G. Y.

Disazo-dyes from 6-Amino-α-naphthol-3 : 7-disulphonic Acid. K. OEHLER (D.R.-P. 158147).—Disazo-dyes resembling those prepared from 6-amino-α-naphthol-3-sulphonic acid (Abstr., 1904, i, 809, and this vol., i, 162) may be prepared from 6-amino-α-naphthol-3 : 7-disulphonic acid, obtained by heating β-naphthylaminetrisulphonic acid with sodium hydroxide at 190°. C. H. D.

Nature of Chemical and Electrical Stimulation. II. The Tension Coefficient of Salts and the Precipitation of Colloids by Electrolytes. ALBERT P. MATHEWS (*Amer. J. Physiol.*, 1905,

14, 203—230).—The precipitation of colloidal albumin is brought about chiefly by an alteration in surface energy, and the precipitating power of an electrolyte is determined primarily by the solution tensions of the ions; ions of the same sign dissolve, and of the opposite sign precipitate, the colloid; their power is inversely proportional to the solution tension. W. D. H.

The Physical Units of Proteid Matter and the part played by Lime in their Coagulation. G. Malfitano (*Compt. rend.*, 1905, **141**, 503—504).—A solution of proteid matter consists of groups formed from complex organic matter associated with phosphates of the alkali or alkali earth metals in an acid or alkaline medium (compare this vol., ii, 14). From such a solution the proteid matter is precipitated by neutralisation, the precipitate always containing varying quantities of calcium phosphate. If, however, the nature of the groups is altered either by prolonged heating of the acid or alkaline solution, or by the action of a diastase, they are no longer precipitated by neutralisation, but are by the addition of large quantities of a normal salt, and they then contain acid or alkali phosphates and a less quantity of calcium phosphate. M. A. W.

Solubility of Globulin (Edestin) in Salt Solutions. Thomas B. Osborne and Isaac F. Harris (*Amer. J. Physiol.*, 1905, **14**, 151—171).—Two forms of solution result where saline solutions are applied to edestin: (1) requires a large amount of salt; the edestin is precipitated unchanged from such a solution by water or dilute acids; (2) requires a small amount of salt; from such a solution the edestin is not precipitated by the reagents mentioned, and the anion has entered into combination with the proteid. Details are given for a large number of salts and their compounds with edestin.

W. D. H.

Composition of Proteid from Pine Seeds. Emil Abderhalden and Yutaka Teruuchi (*Zeit. physiol. Chem.*, 1905, **45**, 473—478).—The proteid obtained from the seeds of *Picea excelsa* on hydrolysis with acids yielded glycine, 0·6; alanine, 1·8; pyrrolidine-2-carboxylic acid, 2·8; leucine, 6·2; glutamic acid, 7·8; aspartic acid, 1·8; phenylalanine, 1·2; serine, 0·08; tyrosine, 1·7 per cent.; also aminovaleric acid and tryptophan. W. D. H.

Composition of Conglutin from Lupin Seeds. Emil Abderhalden and J. B. Herrick (*Zeit. physiol. Chem.*, 1905, **45**, 479—485).—This proteid on hydrolysis with acids yielded glycine, 0·8; alanine, 2·5; aminovaleric acid, 1·1; leucin, 6·75; pyrrolidine-2-carboxylic acid, 2·6; phenylalanine, 3·1; glutamic acid, 9; and aspartic acid, 3 per cent. The analytical methods used are given at some length. W. D. H.

Osmotic Pressure of Hæmoglobin Solutions. E. Waymouth Reid (*J. Physiol.*, 1905, **33**, 12—19).—The fairly constant osmotic pressure in relation to concentration in solutions of once-crystallised hæmoglobin, coupled with the appearances in the ultra-microscope,

leads to the conclusion that this substance when prepared by the methods described in the paper is in a true state of solution.

W. D. H.

Fluorides of Oxyhæmoglobin. ANTONY VILA and M. PIETTRE (*Bull. Soc. chim.*, 1905, [iii], **33**, 1083—1084. Compare this vol., i, 500, 622, and ii, 402).—If the new absorption band is due to methæmoglobin, as Ville and Derrien assert (this vol., i, 622), then it must be assumed that the addition of fluorides to oxyhæmoglobin converts the latter into methæmoglobin, since oxyhæmoglobin solutions show the same absorption band on the addition of fluorides. It is shown that the crystalline substance described by Ville and Derrien (*loc. cit.*) and supposed by them to be a fluorine compound of methæmoglobin is formed in the absence of fluorides and does not contain fluorine.

T. A. H.

The Origin of Cholehæmatin (Bilipurpurin). LEON MARCHLEWSKI (*Zeit. physiol. Chem.*, 1905, **45**, 466—467. Compare Abstr., 1905, i, 500).—Cholehæmatin or bilipurpurin is identical with phylloerythrin. It is recommended that the last name be the one to be retained, as it indicates the origin of the substance from chlorophyll, and not from the blood or the bile.

W. D. H.

Preparation and Analysis of Nucleic Acids. VII. On the Nucleic Acid of the Spleen. PHOEBUS A. LEVENE (*Zeit. physiol. Chem.*, 1905, **45**, 370—380. Compare Abstr., 1903, i, 375, 668; 1904, i, 126; this vol., i, 105).—In the final stages of preparation of the nucleic acid, it is dissolved in excess of concentrated acetic acid and is freed from remaining impurities by precipitation from this solution by copper chloride or hydrochloric acid. The elementary composition of the acid from the spleen is but little different from those from other sources given previously. After hydrolysis, 100 grams yielded 8·3 of adenine picrate, 1·6 of guanine, 5·7 of thymine, 21·4 of cytosine picrate, and small quantities of uracil. By hydrolysis with 5 per cent. sulphuric acid, all the carbohydrate of the molecule is found as soluble decomposition products. If 2 per cent. acid is used, an insoluble substance is obtained in which the proportion of carbohydrate to pyrimidine bases is greater than in the original acid, although the absolute yield of lævulic acid is lower than in hydrolysis of the nucleic acid. A melanin-like substance was also obtained by hydrolysis with strong mineral acids, as already described by Schmiedeberg and by Osborne and Harris.

W. D. H.

Composition of Gelatin impregnated with Potassium Dichromate and rendered Insoluble by Subsequent Exposure to Light. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and ALPHONSE SEYEWETZ (*Bull. Soc. chim.*, 1905, [iii], **33**, 1032—1040. Compare Abstr., 1904, i, 210).—When gelatin, impregnated with potassium dichromate, is exposed to light, a portion of the salt is at once reduced with the formation of chromium sesquioxide and potassium hydroxide. The latter reacts with the excess of the dichromate to form potassium

chromate. This in turn is slowly reduced by the gelatin, forming more chromium sesquioxide, and finally chromium chromate is also probably formed by the action of chromium sesquioxide on the excess of potassium dichromate. In the first of these reactions the gelatin absorbs a constant quantity of about 3·5 per cent. of its weight of chromium sesquioxide to form the insoluble compound already described (*loc. cit.*). The amount subsequently absorbed increases with the concentration of the solution of dichromate used for impregnation and the duration of the subsequent exposure of the impregnated gelatin film to light, but the amount increases more slowly as the potassium chromate accumulates. The maximum amount of chromium compounds absorbed by the gelatin is equal to about 10 per cent. of chromium sesquioxide. Some chromium chromate appears to be formed when chromium sesquioxide is macerated in a solution of potassium dichromate in water. T. A. H.

Composition of Gelatin rendered Insoluble by Exposure to Light in Presence of Chromic Acid or Chromates. Auguste Lumière, Louis Lumière, and Alphonse Seyewetz (*Bull. Soc. chim.*, 1905, [iii], **33**, 1040—1042. Compare preceding abstract).—Chromic acid and ammonium dichromate are both much more readily reduced by gelatin under the influence of light than is potassium dichromate. This is due to the fact that in the cases of the two former substances no stable salt corresponding with potassium chromate is formed. Analyses of the "insoluble gelatin" produced by the action of the foregoing substances and by other dichromates are tabulated in the original. It is noteworthy that in the cases of the dichromates of zinc, barium, lead, aluminium, and iron, the "insoluble gelatin" produced also contains a quantity of the oxide of the metal, the dichromate of which is used for impregnation. T. A. H.

Swelling of β-Gelatin. Wolfgang Ostwald (*Pflüger's Archiv*, 1905, **109**, 277—288).—The name β-gelatin, which was first introduced by M. Traube for a 25 per cent. solution of gelatin which had been heated at 100° until it no longer set, is used by the author in a more general sense to include all gelatin solutions which have been heated. It is found that both the rate and intensity of swelling are greater for β-gelatin than for ordinary gelatin. When account is taken of the increased solubility at higher temperature and with prolonged heating, the curve obtained by plotting the intensity of swelling against the length of time during which the gelatin was heated is similar to that obtained by Schroeder for the viscosity (Abstr., 1903, ii, 721).

The greater swelling capacity of plates of β-gelatin dried at 50° is not to be attributed to the fact that these plates contain a smaller amount of water than similar plates of ordinary gelatin.

β-Gelatin is more soluble than the ordinary, and this solubility begins at a given maximum swelling intensity, after which destruction of the microstructure of the plates probably occurs. J. J. S.

Organic Chemistry.

Mineral Oil from the Torbanite of New South Wales. JAMES M. PETRIE (*J. Soc. Chem. Ind.*, 1905, **24**, 996—1002).—The relationship of torbanite to other bituminous minerals is discussed and its microscopic structure and composition recorded. It contains a very small quantity of natural oil (up to 0·3 per cent.) which can be extracted by prolonged agitation of the pulverised shale with ether. The natural oil resembles vaseline in consistency and has a reddish-brown colour with a dark green fluorescence. It solidifies at 30° and begins to boil at 160°; it has sp. gr. 0·9516 at 20°/4° and *n* 1·5338 at 20°. It consists chiefly of saturated hydrocarbons.

The crude oil resulting from the destructive distillation of torbanite as well as the four fractions (naphtha, solar oil, heavy oil, and residue) obtained by treating the crude oil with sulphuric acid and then with sodium hydroxide and distilling, were subjected to fractional distillation. The volumes, specific gravities, refractive indices, bromine absorption, and substitution values, and in some cases the vapour densities of the various fractions are recorded.

The crude oil is a mixture chiefly of paraffins and olefines. The olefines form about 70 per cent. of the lightest distillate, but the proportion decreases as the boiling point rises, until at 280° the distillate consists almost entirely of paraffins.

The naphtha, which forms 9 per cent. of the crude oil, consists of approximately equal parts of paraffins and olefines with boiling points ranging from 30° to 200° and sp. gr. 0·660—0·800, the paraffins in this fraction ranging from pentane to undecane. The solar oil forms 54 per cent. of the crude oil, boils from 200—270°, and the sp. gr. ranges from 0·800—0·870. It contains 50 per cent. of paraffins in the lightest portion, the proportion increasing to 80 per cent. in the fraction distilling at 270°. The paraffins included range from dodecane to pentadecane.

The heavy oil constitutes 17 per cent. of the crude oil. The lightest portion, boiling between 270° and 300°, contains the last traces of the olefines, together with penta- and hexa-decanes. The paraffins $C_{17}H_{36}$ to $C_{30}H_{62}$ represent the oil boiling above 300°. Chrysene appears at the end of the distillation.

Minute quantities of benzene and its homologues were detected in the crude oil, together with a notable quantity of phenols and a trace of thiophen, and nearly all the distillates deposited pyrrole-red on standing.

The behaviour towards mixtures of sulphuric and nitric acid and the high sp. gr. of the distillates point to the presence of naphthenes in the oil. H. M. D.

Incomplete Combustion of Gases. Cause of the Luminosity of Flame. WILHELM MISTELI (*Chem. Centr.*, 1905, ii, 1075; from *J. Gasbel*, **48**, 802—804. Compare Tanatar, Abstr., 1901, ii, 13, 228).—By the explosion of mixtures of ethylene and electrolytic

gas, the hydrocarbon is resolved into its elements, and traces of methane and acetylene are formed, whilst the oxygen combines with the elements of the hydrocarbon, forming carbon monoxide and hydrogen, carbon monoxide and water, or carbon dioxide and water, according to the proportion present. Explosion only takes place when the requisite quantity of oxygen is present, and the presence of 33 per cent. of ethylene prevents it. Similar results are obtained, broadly speaking, by the incomplete combustion of propylene, acetylene, and methane. The explosion of mixtures of propylene and electrolytic gas occurs when two volumes of oxygen are present, marsh gas and traces of acetylene being formed. The presence of 18 per cent. of propylene completely inhibits combustion. The phenomena appear in this case to be affected by the shape of the explosion vessel.

The explosion of acetylene and electrolytic gas is not dependent on the proportions of the gases, and traces of methane are formed. Acetylene, propylene, and ethylene are decomposed by the action of the electric spark; methane is also decomposed, but with much greater difficulty. The more readily the gas is itself decomposed, the less is the proportion of electrolytic gas required for explosion. Mixtures containing methane behave like those containing propylene and do not explode when 0·5, 1·5, or 2 volumes of oxygen are present; combustion is prevented by the presence of 32 per cent. of the hydrocarbon. Traces of acetylene are formed by the explosion.

In mixtures containing ethylene and acetylene, which are just explosive, the whole of the hydrogen is in the free state, and in the case of the other hydrocarbons almost all the hydrogen is free. The oxygen does not react with the hydrocarbons as such, but combines only with the products of their decomposition. The effect of the hydrocarbons on the inflammability of electrolytic gas depends therefore on their decomposition, the carbon then combining with the oxygen to form carbon monoxide.

Hydrogen cannot be accurately estimated in mixtures of hydrogen and methane or its homologues by explosion, since small quantities of the former escape combustion, but the palladium methods of Winkler, Bunte, and Hempel give accurate results. The hydrogen in mixtures containing hydrocarbons can only be estimated by combustion when but one saturated hydrocarbon of known composition is present.

E. W. W.

Preparation of Halogen Alkyls. Rudolf F. Weinland and Karl Schmid (*Ber.*, 1905, 38, 3696. Compare this vol., i, 557).—The method of preparing methyl chloride by heating dry sodium chloride with methyl sulphate has been already described by Dumas (*Ann. Chim. Phys.*, 1835, 58, 36).

E. F. A.

Preparation of Pure Ethyl Alcohol. Ludwig W. Winkler (*Ber.*, 1905, 38, 3612—3616).—To prepare pure ethyl alcohol, commercial absolute alcohol is shaken with small quantities of finely-divided silver oxide and potassium hydroxide, at the ordinary temperature, for some days, until it does not reduce ammoniacal silver solution, then boiled with 20 grams of calcium filings per litre for

some hours, and finally distilled. The distillate contains about 0·1 per cent. of water, which may be removed by repeating the distillation with calcium filings. The ethyl alcohol so obtained boils at 77·81° under 743·5 mm., or at 78·2° under 754·9 mm., or at 78·29° under 757·8 mm. pressure, and is less hygroscopic than usually stated, as when exposed to the air in an open beaker for 15 minutes, it absorbs less than 0·1 per cent. of water. G. Y.

Methionic [Methanedisulphonic] Acid. GEORG SCHROETER and GUSTAV HERZBERG (*Ber.*, 1905, 38, 3389—3393).—*Methyl methanedisulphonate*, $CH_2(SO_3Me)_2$, obtained from the silver salt and methyl iodide in ethereal or chloroform solution, forms long, white needles, melts at 47°, and is easily hydrolysed by water. The *ethyl* ester is an oil which does not solidify. By acting with potassium and methyl iodide on the methyl or ethyl ester and hydrolysing the product, *barium methylmethionate* [*ethane-aa-disulphonate*], $CHMe(SO_3)_2Ba$, is obtained; using ethyl iodide in place of methyl iodide, *barium ethylmethionate* [*propane-aa-disulphonate*] is formed.

Methanedisulphonic chloride, $CH_2(SO_2Cl)_2$, obtained by the interaction of methanedisulphonic acid and phosphorus pentachloride, boils at 135° under 10 mm. pressure, has a sp. gr. 1·821 at 22°, and solidifies only at low temperatures; it sometimes changes into a solid modification, which melts at about 60°, and is reconverted by distillation into the form melting at low temperatures. The chloride attacks alcohols vigorously, but does not give rise in this case to normal esters. With ethyl aminoacetate, a well-defined crystalline *methanedisulphonyl ethylaminoacetate*, $CH_2(SO_2{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et)_2$, is obtained, which melts at 113·5°. With aniline, the *anilide*, $CH_2(SO_2{\cdot}NHPh)_2$, is produced; it forms lustrous, white crystals, melts at 192—193°, and gives a well-defined crystalline *sodium* derivative and a *barium* derivative,

$$CH_2(SO_2{\cdot}NPh)_2Ba,3H_2O.$$

On digesting the alkaline solution of the anilide with methyl sulphate *methanedisulphonylbismethylaniline*, $CH_2(SO_2{\cdot}NMePh)_2$, is obtained; it crystallises from alcohol in needles and prisms, melts at 141·5—142·5°, and with sodium in benzene gives the *derivative*

$$CHNa(SO_2{\cdot}NMePh)_2.$$

The *compound*, $CH_2(SO_2{\cdot}NEtPh)_2$, is obtained by ethylating the anilide with ethyl sulphate or with ethyl bromide at 100—120°, or by the action of ethylaniline on the chloride; it crystallises from alcohol and melts at 112—114°. In benzene solution it interacts with sodium to form a *sodium* derivative, $CHNa(SO_2{\cdot}NEtPh)_2$, which combines with ethyl bromide or iodide giving *propane-aa-disulphonylbisethylaniline*, $CHEt(SO_2{\cdot}NEtPh)_2$; this crystallises from alcohol in thick, transparent prisms, melts at 135°, and when heated with hydrochloric acid at 180—200° gives ethylaniline and *propane-aa-disulphonic acid*, $CHEt(SO_3H)_2$; the *barium* salt of the latter, $CHEt(SO_3)_2Ba,3H_2O$, forms lustrous scales.

Methanedisulphonylbisphenetidine, $CH_2(SO_2{\cdot}NH{\cdot}C_6H_4{\cdot}OEt)_2$, melts at 221°, the *diethyl* derivative at 141—142°, *propane-aa-disulphonylbisethylphenetidine*, $CHEt(SO_2{\cdot}NEt{\cdot}C_6H_4{\cdot}OEt)_2$, at 93·5—94 5°. W. A. D.

New Method of Preparing Esters. WILLIAM W. TAYLOR (*Proc. Roy. Soc. Edin.*, 1905, **25**, 831—834).—The yields obtained in the preparation of esters are frequently unsatisfactory in consequence of the hydrolysing action of the water formed. In the method described for the preparation of ethyl esters, the water produced is removed by addition of benzene and distillation of the ternary mixture, ethyl alcohol, benzene, and water (compare Young, Trans., 1902, **81**, 707). In the actual working of the process, the dry acid is mixed with an excess of ethyl alcohol, and after addition of 1 c.c. of alcoholic hydrogen chloride, the solution is boiled for 20—30 minutes in a flask provided with a very efficient fractionating column and a tap funnel. A quantity of benzene sufficient to remove one-quarter of the water produced in the reaction is then run in, together with a little ethyl alcohol, and the ternary mixture distilled off. As soon as all the benzene has come over, distillation stops. This process is repeated three times. The residue is then free from water and is transferred to a fractionating flask and distilled under reduced pressure. The method has given good results in the preparation of ethyl tartrate, oxalate, succinate, and benzoate. H. M. D.

Metallic Formates and Acetates. ETTORE COLONNA (*Gazzetta*, 1905, **35**, ii, 224—228).—*Stannous acetate*, $Sn(C_2H_3O_2)_2$, prepared by boiling 100 c.c. of 98 per cent. acetic acid in a reflux apparatus with 90 grams of finely-granulated tin, distils in the form of a feathery mass of long, silky needles, softening at 170°, melting at 181—182°, and boiling at about 238—240°; it dissolves in acetic acid, giving a solution which gradually becomes gelatinous.

Stannous formate, $Sn(CHO_2)_2$, separates in white, silky plates having the form of either a hexagon or parallelogram; it softens at 140—150° and then melts and decomposes. In contact with air, it assumes a yellow colour.

Bismuth acetate, $Bi(C_2H_3O_2)_3$, prepared by protracted boiling of acetic acid with bismuth, separates in hexagonal plates, dissolves in acetic acid, and decomposes without melting.

Bismuth formate, $Bi(CHO_2)_3$, separates in flocks of silky needles and decomposes without melting. T. H. P.

Insoluble Basic Aluminium Acetate. RUDOLF REISS (D.R.-P. 160348).—The basic acetates prepared by heating solutions of aluminium acetate are variable in composition and properties. An insoluble product of constant composition, containing 72 per cent. of acetic acid, is obtained by boiling a 5—15 per cent. solution of aluminium acetate, strongly acidified with acetic acid. The product separates rapidly in a dense form. The same basic acetate is obtained when a neutral 15 per cent. solution of aluminium acetate is heated in an autoclave. C. H. D.

Sulphonalcarboxylic Acids, and the Physiological Activity of Acid and Basic Derivatives of Sulphonal. THEODOR POSNER (*Chem. Zeit.*, 1905, **29**, 1107—1108).—After giving a summary of the

results already published by himself, Baumann, and Autenrieth on the properties of α- and β-disulphone-carboxylic acid, the author draws a comparison between β-ketonic acids and β-disulphone-carboxylic acids, pointing out that whereas the former on hydrolysis yield either ketones or acids, the latter lose a sulphone group leaving a substituted *iso*crotonic acid, for example,

$$CH_3\cdot C(SO_2Et)_2\cdot CH_2\cdot CO_2Et + H_2O = CH_3\cdot C(SO_2Et){:}CH\cdot CO_2H + EtSO_2H + EtOH.$$

This decomposition does not, however, take place when the two hydrogens attached to the α-carbon atoms are replaced by alkyl groups.

The physiological properties of these substances are such as to render them useless for therapeutic purposes. P. H.

Molecular Transpositions and Migration of Carboxyl Group in the Dehydration of Certain Hydroxy-acids. EDMOND E. BLAISE and A. COURTOT (*Compt. rend.*, 1905, **141**, 724—725. Compare Abstr., 1903, i, 604; 1904, i, 366, 796).—When ethyl hydroxypivalate [ethyl β-hydroxy-$\alpha\alpha$-dimethylpropionate] is treated with a dehydrating agent, a mixture of ethyl tiglate and angelate is obtained; this reaction involves a molecular transposition whereby a methyl group and a hydrogen atom change places, and the elements of a molecule of water are removed, according to the equations

$$OH\cdot CH_2\cdot CMe_2\cdot CO_2H \longrightarrow OH\cdot CHMe\cdot CHMe\cdot CO_2H \longrightarrow CHMe{:}CMe\cdot CO_2H.$$

When ethyl β-phenyl-$\alpha\alpha$-dimethylhydracrylate is treated with phosphoric oxide, it is converted into ethyl dimethylatropate [ethyl α-phenyl-$\beta\beta$-dimethylacrylate], the molecular transposition involved in this reaction is a change of places between the carbethoxy- and hydroxyl groups, with the subsequent elimination of the elements of a molecule of water, according to the scheme:

$$OH\cdot CHPh\cdot CMe_2\cdot CO_2Et \longrightarrow CO_2Et\cdot CHPh\cdot CMe_2\cdot OH \longrightarrow CO_2Et\cdot CPh{:}CMe_2.$$

M. A. W.

Thallium Oxalates. RICHARD ABEGG and JAMES F. SPENCER (*Zeit. anorg. Chem.*, 1905, **46**, 406—414).—The solubility of thallous oxalate at 25° was determined, and also the change of solubility caused by the addition of thallium nitrate and of potassium oxalate. In accordance with the Nernst theory, the solubility in presence of thallium nitrate diminishes owing to the increase of the thallium ions; it diminishes also at first in presence of small quantities of potassium oxalate, but afterwards increases considerably, owing to the formation of a complex salt. Attempts to determine the ionic concentration of the $Tl^{\cdot}$ ion failed, but the C_2O_4'' concentration was determined with the aid of Schäfer and Abegg's $Ag \mid Ag_2C_2O_4$ electrode. This electrode in a solution of 0·5 mol. $K_2C_2O_4$ (containing, according to its conductivity, 0·288 mol. C_2O_4'') has an *E.M.F.* of +0·143 volt against a 1/10-normal electrode. The following

formula is used to calculate the C_2O_4'' concentration x of the solutions from the *E.M.F.* ϵ opposed to the 1/10 normal electrode:

$$0·143 - \epsilon = 0·0295\log(x/0·288).$$

The solubility product $(Tl^{\cdot})^2(C_2O_4'')$ was thus found $= 1·38·10^{-5}$, and the stability constant $k = TlC_2O_4'/Tl^{\cdot}C_2O_4'' = 108$.

The solubility curves for mixtures of thallous oxalate, with thallium nitrate and potassium oxalate respectively are given, together with calculations of the ionic concentration in certain selected cases.

Quantitative experiments showed that even concentrated solutions of potassium oxalate dissolve very little thallic oxalate, so that the tendency to the formation of complex ions is small. Attempts to determine the $Tl^{\cdot\cdot\cdot}$ concentration from measurements of the oxidation potential failed, but incidentally showed that the thallic salt is self-reducing at the expense of the oxalate ions. The vigorous evolution of carbon dioxide is easily shown on warming a flask in which moist thallic oxalate has been placed; at the same time, white thallous oxalate and brown thallic hydroxide are formed. D. H. J.

Esterification Experiments. ALEX. D. BOGOJAWLENSKY and J. NARBUTT (*Ber.*, 1905, **38**, 3344—3353).—The effect of the introduction of various metallic salts on the esterification of organic acids by ethyl alcohol has been studied. The salts employed were ferrous, zinc, cobalt, cupric, sodium, manganous, and nickel sulphates, also potassium pyrosulphate and chabazite.

Experiments made with succinic acid, using the acid, sulphate, and alcohol in the proportions 1 : 1·25 : 4 and boiling for about four hours, show that as regards their efficiency the salts may be arranged in the order ferrous, nickel, cupric, manganous, cobalt, and zinc sulphates. Sodium sulphate has no accelerating action. Copper sulphate accelerates the esterification of other aliphatic acids such as acetic, *n*-butyric, *iso*valeric, and citric acids; the acceleration is further increased by the addition of a little free sulphuric acid. Potassium pyrosulphate gives extremely good results with aromatic acids such as benzoic, salicylic, *o*-nitrobenzoic, gallic, cinnamic, and mandelic acids, whereas copper sulphate is not advantageous. The sulphates were dehydrated at 100°; their action may be partly due to their hygroscopic nature and partly to the small amount of free acid to which they give rise.

Copper sulphate is of no use for the esterification of trimethylcarbinol with acetic acid. Salol cannot be obtained by using potassium pyrosulphate and α- and β-naphthols cannot be esterified by this reagent. J. J. S.

Tetra-amminechromium Salts. PAUL PFEIFFER (*Ber.*, 1905, **38**, 9352—3601. Compare this vol., i, 33).—[With S. BASCI.]—Chloroaquotetra-amminechromium chloride (Jörgenson, Abstr., 1890, 1213) is formed by the action of 25 per cent. aqueous ammonia on diaquodihydroxylodipyridinechromium chloride (Abstr., 1902, i, 729) at 45—48°, and treatment of the resulting solution with concentrated hydrochloric acid; with ammonium sulphate in aqueous solution, it yields the characteristic oxalate; with potassium oxalate, the *oxalate*,

$[(NH_3)_4Cr(H_2O)Cl]C_2O_4$, which separates in violet crystals, gives a precipitate of calcium oxalate with calcium chloride in aqueous solution, and yields silver chloride quantitatively when boiled with silver nitrate in nitric acid solution.

Bromoaquotetra-amminechromium bromide (Cleve) is formed by the action of 25 per cent. aqueous ammonia and concentrated hydrobromic acid on diaquodihydroxylodipyridinechromium chloride; it forms violet, glistening crystals, and with potassium oxalate in aqueous solution yields a violet precipitate.

Oxalatotetra-amminechromium iodide, $[(NH_3)_4CrC_2O_4]I,H_2O$, is formed by the successive action of ammonium oxalate and potassium iodide on chloroaquotetra-amminechromium chloride in aqueous solution; it crystallises in stout, glistening, orange-red prisms, loses H_2O over phosphoric oxide in a desiccator, and gradually decomposes at 100°. The *bromide*, $[(NH_3)_4CrC_2O_4]Br,\frac{1}{2}H_2O$, is formed by the action of concentrated hydrobromic acid on the nitrate; it crystallises in orange leaflets and dissolves in water to form an orange solution, which becomes green when warmed.

The action of ammonium oxalate and hydrobromic acid on chloroaquotetra-amminechromium chloride leads to the formation of Cleve's triamminechromium oxalate.

Oxalatotetra-amminechromium chloride, $[(NH_3)_4CrC_2O_4]Cl$, is formed by the action of concentrated hydrochloric acid on the nitrate in aqueous solution; it crystallises in glistening, orange leaflets, does not form a precipitate with calcium chloride in aqueous solution at the ordinary temperature, but is decomposed by boiling calcium chloride solution, and gives a precipitate with silver nitrate in nitric acid solution at the ordinary temperature. In concentrated aqueous solution, the chloride forms precipitates with platinic chloride, potassium dichromate and chromate, sodium dithionate, potassium iodide, and concentrated nitric acid. The *nitrate*, $[(NH_3)_4CrC_2O_4]NO_3,H_2O$, is formed by the successive action of ammonium oxalate and potassium nitrate on chloroaquotetra-amminechromium chloride; it crystallises in glistening, orange-red needles, is less soluble in water than are the bromide and chloride, and in concentrated solution forms with potassium chromate or dichromate a precipitate consisting of glistening, orange needles, and, with potassium iodide, stout, orange crystals. When warmed with concentrated hydrochloric or hydrobromic acid, the nitrate dissolves to form red solutions which, on cooling, deposit chloroaquotetra-amminechromium chloride and bromoaquotetra-amminechromium bromide respectively. G. Y.

Syntheses with Ethyl Sodiomalonate and Similar Compounds. Arthur Michael (*Ber.*, 1905, **38**, 3217—3234. Compare this vol., i, 195, 506).—The action of ethyl chloroacetate on ethyl sodiomalonate in ethereal solution leads to the formation of a colourless, neutral solution and a precipitate consisting of sodium chloride, but in benzene solution, slowly at the laboratory temperature, more quickly on boiling, to the formation of a reddish-yellow, neutral solution, which is slightly opalescent in transmitted light, together with only traces of sodium chloride. This solution decomposes with

separation of sodium chloride, rapidly on addition of traces of water, or more slowly on treatment with methyl or ethyl alcohol; it decomposes to only a slight extent at 150° in a sealed tube, whilst at 200° sodium chloride separates quantitatively. It is not attacked by anhydrous carbon dioxide, but is decomposed with formation of sodium chloride when treated with hydrogen chloride; it yields sodium chloride together with a small quantity of a *substance* which crystallises in groups of needles when treated with glacial acetic acid, and it is decomposed also by the action of acetyl chloride, iodine, or silver benzoate. The yellowish-red, viscid liquid, $C_{11}H_{18}O_6ClNa$, obtained on evaporating the solution at 40° and finally on the water-bath, decomposes slowly in a vacuum at the laboratory temperature, more quickly at 100°.

The *additive* compound of ethyl chloroacetate and ethyl sodioethylmalonate, $C_{13}H_{22}O_6ClNa$, is formed in ethereal or benzene solution; the viscid, red oil obtained on evaporation decomposes with formation of sodium chloride when treated with absolute methyl or ethyl alcohols, more slowly with ethyl acetate or chloroform. The neutral ethereal solution is yellow and opaque by reflected, chrome-yellow by transmitted light, is only slowly decomposed at 100° in a sealed tube, but decomposes immediately on addition of traces of water; the yellow neutral benzene solution becomes orange at the ordinary temperature, or red when heated on the water-bath, and is decomposed by moisture, iodine, acetyl chloride, or hydrochloric acid.

The action of ethyl chloroacetate on ethyl sodiomethylmalonate in benzene solution leads to the formation of a yellow solution, which becomes orange when heated on the water-bath and on evaporation yields a viscid *oil*. The *additive* compound of ethyl chloroacetate and ethyl sodiopropylmalonate is formed in ethereal benzene solution, and, on evaporation, is obtained as a red, viscid oil. These derivatives of methyl- and propyl-malonic acids have properties resembling those of the corresponding ethyl compound.

The action of ethyl chloroacetate on ethyl sodioacetoacetate in warm ethereal solution leads to the formation of sodium chloride, but in benzene solution to the formation of a slightly alkaline orange solution, which deposits sodium chloride on addition of traces of water, but only slowly on treatment with methyl or ethyl alcohol, ether, ethyl acetate, or chloroform. The *additive* compound is obtained on distillation of the benzene and heating the residue at 110° under 12 mm. pressure as a viscid, orange, slightly milky liquid, which dissolves unchanged in benzene, but is less stable towards methyl or ethyl alcohol, ether, ethyl acetate, or chloroform than are the corresponding malonate derivatives.

The *additive* compound of ethyl chloroacetate and ethyl sodioethylacetoacetate is formed in ethereal solution and is obtained, on evaporation, as a red, viscid liquid; it is decomposed immediately by water, but dissolves in methyl alcohol or ethyl acetate to form a clear solution which decomposes only gradually.

Comparative experiments show that the action of alkyl iodides on sodio-derivatives of ethyl acetoacetate or malonate, as expressed by the changes of temperature, takes place more rapidly than on sodium alkoxides. Of the results given, the following may be quoted in

illustration. An excess, 5·8 grams, of methyl iodide was added to 0·95 gram of sodium in 12·5 grams of propyl alcohol I; to 0·49 gram of sodium in 10 grams of ethyl alcohol together with 2·5 grams of ethyl lactate II; to 0·36 gram of sodium in 10 grams of ethyl alcohol together with 2·5 grams of ethyl malonate III; to 0·31 gram of sodium in 10 grams of ethyl alcohol together with 2·5 grams of ethyl ethylmalonate IV, and the temperature taken at intervals after mixing.

Minutes after mixing.	I.	II.	III.	IV.
2	2°	1°	32°	10°
4	6	2	28	25
6	22	3	24	23
10	41	6	19	19
20	25	8·5	10	10
30	17	8	7	7

G. Y.

Butadiene Compounds. VII. The Colour of the Fulgenic Acids and Fulgides. HANS STOBBE (*Ber.*, 1905, **37**, 3673—3682). —[With ALFRED LENZNER.]—$\alpha\alpha\delta\delta$-Tetramethylfulgenic acid,

$$CMe_2{:}C(CO_2H){\cdot}C(CO_2H){:}CMe_2,$$

prepared by the gradual addition of a mixture of ethyl teraconate and acetone to a suspension of sodium ethoxide in ether, is a colourless, crystalline compound melting and decomposing at 230°. *Tetramethylfulgide*, $\begin{matrix}CMe_2{:}C{\cdot}CO\\ \vert \\ CMe_2{:}C{\cdot}CO\end{matrix}\!\!>\!O$, formed by dissolving the corresponding acid in cold methyl chloride, crystallises in colourless plates melting at 59·5°.

[With ROBERT ROSE and FERDINAND GADEMANN.]—*δ-Phenyl-$\alpha\alpha\delta$-trimethylfulgenic acid* crystallises in colourless needles or six-sided prisms melting at 208—210°; at the same time a stereoisomeride melting at 221—223° is formed, which yields a more easily soluble *barium* salt. *δ-Phenyl-$\alpha\alpha\delta$-trimethylfulgide* crystallises from light petroleum in citron-yellow needles melting at 132—133°.

[With ALFRED LENZNER.]—*$\delta\delta$-Diphenyl-$\alpha\alpha$-dimethylfulgenic acid*, $CPh_2{:}C(CO_2H){\cdot}C(CO_2H){:}CMe_2$, is obtained as a colourless substance, which, on heating, softens at 188° and melts and decomposes at 201°; the *ester acid* crystallises in colourless prisms, which melt and decompose at 137·5°. *$\delta\delta$-Diphenyl-$\alpha\alpha$-dimethylfulgide* crystallises in six-sided, citron-yellow plates melting at 171·5°. *$\alpha\alpha\delta\delta$-Tetraphenylfulgenic acid*, prepared from benzophenone and ethyl diphenylitaconate, was not obtained pure; the corresponding *tetraphenylfulgide* crystallises in blood-red, triclinic crystals melting at 219°; at the same time, a bright red, rhombic isomeride is formed. E. F. A.

Butadiene Compounds. VIII. Colourless Alkylfulgides. HANS STOBBE and KARL LEUNER (*Ber.*, 1905, **38**, 3682—3685).—*$\delta\delta$-Dimethyl-α-*iso*propylfulgenic acid*, $CMe_2{:}C(CO_2H){\cdot}C(CO_2H){:}CH{\cdot}CHMe_2$, prepared by the condensation of *iso*butyraldehyde and ethyl tetraconate, is a colourless, crystalline compound melting and decomposing at 226°. *$\delta\delta$-Dimethyl-α-*iso*propylfulgide*, formed on dissolving the acid in acetyl chloride, crystallises in colourless platelets melting at 72°. E. F. A.

Mixed Derivatives of *d*-Camphoric Acid and β-Campholide. ALBIN HALLER and GUSTAV BLANC (*Compt. rend.*, 1905, **141**, 697—701).—*a-Methyl camphorate β-chloride*, $COCl\cdot C_8H_{14}\cdot CO_2Me$, prepared by the action of phosphorus trichloride or thionyl chloride on α-methyl β-hydrogen camphorate, is a colourless, mobile liquid, which decomposes into camphoric anhydride and methyl chloride on distillation, is converted quantitatively into dimethyl camphorate by the action of methyl alcohol, reacts with ammonia to form *α-methyl β-camphoramate*, $NH_2\cdot CO\cdot C_8H_{14}\cdot CO_2Me$, a white, crystalline substance, melting at 139°, having $[\alpha]_D$ +57°15′ at 27°, soluble in alcohol, and sparingly soluble in water; and with phenylhydrazine to form *α-methyl β-phenylhydrazocamphorate*, $N_2H_2Ph\cdot CO\cdot C_8H_{14}\cdot CO_2Me$, which melts at 158° and has $[\alpha]_D$ +42°8′ at 26°.

β-Methyl α-hydrogen camphorate, readily obtained by the action of alcoholic potassium hydroxide on dimethyl camphorate, yields *β-methyl camphorate α-chloride* by the action of phosphorus trichloride or thionyl chloride, from which *β-methyl-α-camphoramate* is obtained in the form of beautiful, white crystals melting at 148°, and having $[\alpha]_D$ +23°20′ at 25°.

β-Campholide, $C_8H_{14}<\begin{matrix}CO-\\CH_2\end{matrix}>O$, isomeric with α-campholide, $C_8H_{14}<\begin{matrix}CH_2\\CO-\end{matrix}>O$ (compare Haller, Abstr., 1896, i, 385; Baeyer and Villiger, Abstr., 1900, i, 133; Blanc, this vol., i, 115), obtained by reducing β-methyl α-hydrogen camphorate with sodium in alcoholic solution, crystallises from a mixture of ether and light petroleum in white crystals melting at 218—220°, has $[\alpha]_D$ +39°20′ at 15°, is readily soluble in alcohol or ether, and sparingly soluble in light petroleum. The yield of β-campholide is very poor, and attempts to convert it into β-camphor through β-cyanocampholic acid and β-homocamphoric acid were unsuccessful. M. A. W.

Action of Hydroxylamine on Ethyl Acetylmalonate. F. CARLO PALAZZO and N. SALVO (*Atti Real. Accad. Lincei*, 1905, [v], **14**, ii, 252—255).—The action of hydroxylamine on ethyl acetylmalonate leads to the formation of the compound $C_7H_9O_4N$, melting at 166° and previously obtained by the action of hydroxylamine on ethyl dimethylpyronedicarboxylate (compare Palazzo, Abstr., 1904, i, 762); for this compound, however, the authors suggest the constitution $\begin{matrix}N:CMe\\ | \\ O—CO\end{matrix}>CH\cdot CO_2Et$ as being more probable. T. H. P.

Action of Hydroxylamine on Ethyl Diacetylmalonate. F. CARLO PALAZZO and E. CARAPELLE (*Atti R. Accad. Lincei*, 1905, [v], **14**, ii, 287—289).—The action of hydroxylamine on ethyl diacetylmalonate yields the compound $C_7H_9O_4N$ (compare preceding abstract), an acetyl group being first removed as acethydroxamic acid from the diacetyl ester by the hydroxylamine, which here acts as a hydrolyst. T. H. P.

Dihydroxyglutaric Acids. HEINRICH KILIANI and PETER LOEFFLER (*Ber.*, 1905, **38**, 3624—3626).—αγ-Dihydroxyglutaric acid

from *iso*saccharin (this vol., i, 739) yields a *quinine* salt, which crystallises from water in long, glistening needles. It contains $4H_2O$ and melts at 162°. The quinine salt of *l*-trihydroxyglutaric acid from arabinose contains $5H_2O$ and melts at 180°.

αβ-Dihydroxyglutaric acid has been prepared by the oxidation of glutaconic acid with 1 per cent. potassium permanganate at 0° (yield 5 per cent.), and also by the action of calcium carbonate and water on glutaconic acid dibromide (yield 14 per cent.). The acid crystallises in slender needles or compact prisms, is anhydrous and optically inactive, and melts and decomposes at 164°. It can be titrated with standard alkali, yields a *quinine* salt which crystallises in large, glistening needles, and also a crystalline *potassium hydrogen* salt. The normal *sodium* and *zinc* salts have been obtained in an amorphous condition only.

An αβ-dihydroxyglutaric acid has been prepared by the oxidation of *meta*saccharopentose (Abstr., 1903, i, 10) with dilute nitric acid at 35°. It crystallises in needles or plates, melts at 156°, has $[\alpha]_D$ +11°, is anhydrous, and shows no tendency to lactone formation. Solutions of the alkali salts give no precipitate with barium, strontium, zinc, copper, or cadmium salts. The *potassium hydrogen* salt crystallises from aqueous alcohol in microscopic prisms. The *quinine* salt crystallises in long needles, contains $7H_2O$, and melts at 158—160°.

J. J. S.

Digitalonic Acid. HEINRICH KILIANI (*Ber.*, 1905, **38**, 3621—3623). Compare Abstr., 1902, 1241).—When the lactone of digitalonic acid is oxidised with concentrated nitric acid at 35°, the chief products are oxalic and *αβγ-trihydroxyadipic acid*, $C_6H_{10}O_7$. The *calcium* salt of the latter is soluble in both hot and cold water, but is precipitated on the addition of alcohol. The *quinine* salt crystallises from water in colourless needles, contains $6H_2O$, and melts at 128—130°. The acid obtained from the quinine salt crystallises from water in compact plates melting at 123—124°. The *zinc* salt, $C_6H_8O_7Zn,4H_2O$, and *cupric* salt, $+4H_2O$, have been obtained in a crystalline form.

The differences between this trihydroxyadipic acid and that from *meta*saccharin (Abstr., 1885, 745) are so considerable that it is concluded that they must be structurally isomeric. The acid from digitalonic acid is thus αβγ-trihydroxyadipic acid,

$$CO_2H[CH\cdot OH]_3\cdot CH_2\cdot CO_2H,$$

and digitalonic acid is either $CH_3\cdot[CH\cdot OH]_4\cdot CH_2\cdot CO_2H$ or

$$CH_3\cdot CH(OH)\cdot CH_2\cdot[CH\cdot OH]_2\cdot CO_2H.$$

J. J. S.

Formaldehyde. I. Formaldehyde in Aqueous Solution. FRIEDRICH AUERBACH and HERMANN BARSCHALL (*Chem. Centr.*, 1905, ii, 1081—1083; from *Arb. Kais. Ges.-A.*, **22**, 584—629).—Aqueous solutions of formaldehyde are prepared by subliming trioxymethylene in a stream of nitrogen and absorbing the vapour in water. Lumière and Seyewetz' method (Abstr., 1903, i, 150) may be used for the analysis of the solutions if the correction for the hydrolysis of the sulphate solution is properly applied. Romijn's method is better adapted for small quantities of dilute solutions if the following

conditions are observed. Pure alkali hydroxide, preferably prepared from the metal, should be used, the solution of iodine and alkali should not be mixed before adding the aldehyde, the addition of too much acid is to be avoided, and the liquid should be continuously shaken during the titration with sodium thiosulphate. If an insufficient quantity of iodine is used in the first instance, this cannot be remedied by adding more after the titration. The oxidation of the aldehyde appears to be entirely effected by the hypoiodite formed by the action of the iodine on the alkali hydroxide. The agitation of the solution during the titration is necessary to avoid the action of the thiosulphate on the acid.

The sp. gr. of pure aqueous solutions of formaldehyde at 18° is given in the original paper, and the relationship of the average molecular weight of the aldehyde in its aqueous solution to the concentration has been determined. By means of the application of the law of mass action to the data obtained, it is shown that an equilibrium is established between the molecules of formaldehyde, CH_2O, and those of the polymeride, $(CH_2O)_3$. A better agreement between the observed and calculated values is obtained, however, when it is assumed that both forms are hydrated, methylene glycol being formed from the aldehyde, CH_2O. This assumption does not preclude the possibility of the occurrence of very small quantities of higher polymerides in very concentrated solutions, and in fact the deviations shown by solutions of 37—38 volumes per cent. point to this explanation. The reaction between the two forms in aqueous solutions is reversible, and the equilibrium is attained in a short time when either gaseous formaldehyde or the polymeride is dissolved. As the temperature is raised, the latter tends to decompose into the simpler form, this change being accompanied by absorption of heat. Foelsing's (*Zeit. öffentl. Chem.*, 1904, 322) statements in reference to the effect of the preservative "sterilisol" and the difference shown by solutions prepared in a vacuum do not correspond with the facts, the composition of solutions which have been allowed to remain for a few hours being independent of the method of preparation.

When solutions of formaldehyde are distilled, the distillate is always weaker, and the residue stronger. The boiling point of aqueous solutions decreases with the concentration, and all solutions containing more than 30 vols. per cent. boil at practically the same temperature, hence on distillation a distillate of a higher boiling point is obtained (compare Konowaloff, Abstr., 1881, 1093). The relationships of the composition of the vapour from boiling formaldehyde solutions to the quantity of aldehyde in the solution, and the partial pressure of the aldehyde in solutions at 100° have been determined. The partial pressure in solutions at 18° has been estimated by means of a current of air. Since these methods gave very low values, it would appear that only a very small portion of the aldehyde is contained in the solution in the form of the simple molecule CH_2O. From the partial pressures, the quantities of aldehyde which would be contained in a given volume of saturated vapour at 18° have been calculated. In the case of the strongest solution, which contained 33·8 vols. per cent., it was found that the quantity was only 0·66 gram,

and for the commercial 40 per cent. solution in methyl alcohol less than 1 gram. In practice, however, complete saturation of the vapour is never attained. E. W. W.

Action of Ammonia and of Amines on Chloral. Mitsuru Kuhara and Yoshinori Kishi (*Mem. Coll. Sci. Eng. Kyōto*, 1904—1905, **1**, 114—124).—The action of ammonia on chloral in the free state and in chloroform solution at various temperatures has been examined. The observations indicate that chloral ammonia is the first product, but that this is decomposed either (1) by rise of temperature or (2) by the action of an excess of ammonia into chloroform and formamide according to the equations: (1) $CCl_3 \cdot CH(OH) \cdot NH_2 = CHCl_3 + CHO \cdot NH_2$; (2) $CCl_3 \cdot CH(OH) \cdot NH_2 + NH_3 = CHCl_3 + CH(NH_2)_2 \cdot OH = CHCl_3 + NH_3 + CHO \cdot NH_2$. The aliphatic amines are supposed to react similarly towards chloral, and the entirely different behaviour of the aromatic amines which yield trichloroethylidene derivatives is ascribed to their much weaker basic properties. If aromatic amines are treated with chloral ammonia instead of with chloral, formyl derivatives of the amines are, however, obtained. In this reaction, the chloral ammonia first decomposes into chloroform and formamide, the latter then reacting with the amine. A number of formyl derivatives of aromatic amines were prepared according to this method. H. M. D.

Condensation of *iso*Propylacetaldehyde [*iso*Valeraldehyde] with Acetaldehyde. Bruno Ehrenfreund (*Monatsh.*, 1905, **26**, 1003—1010).—The condensation of *iso*valeraldehyde (Rainer, this vol., i, 16) with acetaldehyde in presence of potassium carbonate has been re-investigated, as the *iso*valeraldehyde used by Wogrinz (Abstr., 1901, i, 254; 1903, i, 604) contained at least α-methylbutaldehyde in addition.

The aldol, $CH_2Pr^{\beta} \cdot CH(OH) \cdot CH_2 \cdot COH$ or $OH \cdot CHMe \cdot CHPr^{\beta} \cdot COH$, is now found to boil at 85° under 15 mm. pressure, and on oxidation with potassium permanganate to form, in addition to *iso*valeric acid, a *hydroxy-acid*, $C_7H_{14}O_3$.

The unsaturated aldehyde, $CH_2Pr^{\beta} \cdot CH \colon CH \cdot COH$ or $CHMe \colon CPr^{\beta} \cdot COH$, is obtained best by heating the aldol with sodium acetate; on oxidation, it yields *iso*valeric acid, oxalic acid, and only a small amount of acetic acid. Reduction of the unsaturated aldehyde with iron filings and acetic acid leads to the formation of a product which is probably identical with Grimshaw's *iso*hexylcarbinol (this Journal, 1873, 313), and on oxidation with potassium permanganate yields *iso*heptoic acid boiling at 211—214°.

In other respects, the properties of the substances obtained agree with those described by Wogrinz (*loc. cit.*). G. Y.

Action of Lead and Bismuth Salts on the Rotatory Power of Sugars, Polyhydric Alcohols, and Hydroxy-acids. II. Hermann Grossmann (*Zeit. Ver. deut. Zucker-Ind.*, 1905, **596**, 941—976. Compare this vol., i, 415).—The results of the author's

investigations on a large number of sugars, polyhydric alcohols, and hydroxy-acids show that most of these compounds readily react with alkaline solutions of lead salts, the hydrogen atoms of the hydroxyl groups being replaced by lead oxide. Owing to the change produced in the optically active molecule by the influence of the heavy lead atom, the formation of these complexes is often accompanied by a change in the sense of the rotation. The alkali necessary for the solution of the insoluble lead compounds at first produced frequently influences the rotation very greatly, especially with tartaric and quinic acids. The lead-alkali compounds of the hexoses are, in general, possessed of but little stability, the free alkali very soon producing intra-molecular changes.

A solution of bismuth nitrate in glycerol and water exerts, on addition of an alkali hydroxide, an influence on the rotation of tartaric acid, with which, together with the dextrorotatory complexes present in alkaline solution, strongly lævorotatory complexes, only stable in presence of hydrogen ions, are formed. Saccharic acid is converted by alkaline bismuth solution into a strongly dextrorotatory substance.

The dextrorotation of mannitol produced by bismuth nitrate, is greater in aqueous solution than when glycerol is added. Of the sugars, only lævulose and invert sugar are appreciably influenced in rotation by alkaline bismuth nitrate solution. The rotations of arabinose, galactose, dextrose, sucrose, lactose, maltose, and raffinose are diminished by alkaline bismuth nitrate solutions, but the change is here ascribed to the excess of alkali present, since increase of the amount of bismuth salt is not accompanied by a corresponding change in the rotation. The same probably holds in the case of quinic acid.

T. H. P.

Acetosulphate of Cellulose. II. CHARLES F. CROSS, EDWARD J. BEVAN, and JOHN F. BRIGGS (*Ber.*, 1905, **38**, 3531—3538. Compare this vol., i, 512).—Particulars are given of the preparation of three series of acetylcellulose sulphuric esters and their salts, the proportions of combined sulphuric acid being 5—6, 9—10, and 25 per cent.; analyses are given of each series of compounds. T. M. L.

Diaminoethyl Ether. SIEGMUND GABRIEL (*Ber.*, 1905, **38**, 3411—3414).—The product formerly obtained by the author (Abstr., 1888, 439, 668, 1267), which Knorr (*Ber.*, 1904, **37**, 3515) has considered to be piperazine picrate, is not identical with the latter prepared directly from piperazine; the substance obtained in this way forms lemon-yellow plates and darkens between 255° and 280° without melting. The substance formerly considered to be the picrate of a base $C_4H_{12}ON_2$ is perhaps *diaminoethyl ether picrate.*

Diphthaliminoethyl ether, $(C_8H_4O_2{:}N{\cdot}CH_2{\cdot}CH_2)_2O$, prepared by heating di-iodoethyl ether (Sand, Abstr., 1901, i, 458 and 741) with potassium phthalimide, crystallises from alcohol in flat rhombohedra, melts at 156·5°, and when heated with hydrochloric acid and acetic acid at 140° gives *diaminoethyl ether hydrochloride*,

$$O(CH_2{\cdot}CH_2{\cdot}NH_2,HCl)_2.$$

This crystallises from 96 per cent. alcohol in long, flat needles and melts at 226—227°. The corresponding *platinichloride*,

$$C_4H_{12}ON_2,H_2PtCl_6,$$

decomposes at 230°. *Diaminoethyl ether* boils at 183—184° and gives a *picrate* which decomposes at 228°. The picrate formerly described decomposed at 218°, so that its identity with the preceding picrate is not yet certain. W. A. D.

Transformation of β-Vinylacrylic Acid into Diaminovaleric Acid. EMIL FISCHER and KARL RASKE (*Ber.*, 1905, **38**, 3607—3612. Compare Fischer and Schlotterbeck, Abstr., 1904, i, 549).—When heated with saturated aqueous ammonia at 150° in a closed vessel, β-vinylacrylic acid yields a *diaminovaleric acid* which, after purification by conversion into the phosphotungstate, is obtained as a dark yellow syrup. It is easily soluble in water or methyl alcohol, has a strongly alkaline reaction in aqueous solution, is precipitated by mercuric chloride, and with phosphotungstic acid forms in aqueous solution a voluminous, or in sulphuric acid solution, a granular precipitate. The diamino-acid does not yield the dibenzoyl derivative characteristic of ornithine, but it may be a mixture, possibly containing small quantities of ornithine, as it forms two crystalline *picrates*, $C_5H_{12}O_2N_2(C_6H_3O_7N_3)_2$, which melts at 185° (corr.), and

$$C_5H_{12}O_2N_2,C_6H_3O_7N_3,$$

which commences to decompose at 130°, and is melted at 160—170° (compare Schulze and Winterstein, Abstr., 1902, i, 231). When distilled under reduced pressure, the diamino-acid forms an *anhydride*, C_5H_7ON, which crystallises in colourless, stout needles, melts at 51—53° (corr.), and is easily soluble in water, ethyl alcohol, ethyl acetate, benzene, or pyridine, and has a slight acid reaction in aqueous solution; when heated with aqueous barium hydroxide at 100°, it yields an *amino*-acid, the aqueous solution of which dissolves copper oxide. The formation of the anhydride shows that the diaminovaleric acid probably has an amino-group in the γ- or δ-position. G. Y.

Synthesis of Polypeptides. XIII. Chlorides of Amino-acids and Polypeptides, and their Use as Synthetical Agents. EMIL FISCHER (*Ber.*, 1905, **38**, 2914—2925. Compare Abstr., 1903, i, 465, 607, 799, 800; 1904, i, 652, 771, 867, 890, 917; this vol., i, 30, 31, 263, 637).—The author has already shown that many amino-acids, when agitated with a mixture of acetyl chloride and phosphorus pentachloride, form compounds of the type $NH_3Cl\cdot CHR\cdot COCl$. It is now shown that all simple amino-acids can be converted into the corresponding chloro-derivatives under suitable experimental conditions. The reaction has been extended to leucylglycine and to leucylglycylglycine; the resulting products combine with esters of amino-acids to form esters of higher polypeptides, which on hydrolysis are converted into the corresponding peptides. The method has been of particular advantage for the syntheses of optically active polypeptides.

Glycyl chloride hydrochloride, $NH_3Cl\cdot CH_2\cdot COCl$, is prepared as follows. Glycine is precipitated from its aqueous solution by the

addition of a large excess of absolute alcohol, dried at 100°, and, when finely powdered, mixed with acetyl chloride. The mixture is cooled to 0° and phosphorus pentachloride gradually added, and the whole agitated for several hours. The hydrochloride is crystalline and is readily converted by ethyl alcohol into glycine ethyl ester hydrochloride.

The action of a mixture of phosphorus pentachloride and acetyl chloride on glycine which has been crystallised from water is different, other substances besides glycyl chloride hydrochloride which are not transformed by alcohol into glycine ethyl ester being formed. The author suggests the possibility of glycine existing in isomeric forms.

For the preparation of *d*-alanyl chloride hydrochloride, it was also found advisable to precipitate the *d*-alanine from its aqueous solution by means of absolute alcohol. d-*Alanyl chloride hydrochloride*, $NH_3Cl\cdot CHMe\cdot COCl$, prepared by the action of a mixture of phosphorus pentachloride and acetyl chloride on *d*-alanine is a crystalline powder. The aqueous solution has $[\alpha]_D$ +7·23° at 20°, whilst *d*-alanine hydrochloride has +9·55°. During the chlorination, racemisation to the extent of about 25 per cent. had accordingly taken place.

Phenylalanyl chloride hydrochloride, $CH_2Ph\cdot CH(NH_3Cl)\cdot COCl$, is a powder.

Leucylglycyl chloride hydrochloride,

$$C_4H_9\cdot CH(NH_3Cl)\cdot CO\cdot NH\cdot CH_2\cdot COCl,$$

prepared by the action of phosphorus pentachloride and acetyl chloride on leucylglycine, is a solid, as also is *leucylglycylglycyl chloride hydrochloride*,

$$C_4H_9\cdot CH(NH_3Cl)\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot COCl,$$

prepared from leucylglycylglycine.

Phenylalanylglycine, $CH_2Ph\cdot CH(NH_2)\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, prepared by the action of phenylalanyl chloride hydrochloride on glycine ethyl ester in chloroform solution, and subsequent saponification of the resulting ester, forms colourless plates and melts and decomposes at about 273° (corr.); it is sparingly soluble in ethyl alcohol, and may also be prepared by the action of α-bromohydrocinnamyl chloride on glycine.

d-*Alanylglycine*, prepared by hydrolysis of the ester formed by the action of *d*-alanyl chloride on ethyl glycine in chloroform solution, separates from a mixture of alcohol and water in needles or in feathery crystals. It melts and decomposes at about 235° (corr.). It is the optical isomeride of the *l*-alanyl glycine, formerly described, and has $[\alpha]_D$ +50·2° at 20° in aqueous solution, a value slightly higher than that observed for the *l*-isomeride.

A new synthesis of leucylglycylglycine ethyl ester,

$$C_4H_9\cdot CH(NH_2)\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et,$$

by the action of leucylglycyl chloride hydrochloride on glycine ethyl ester, is recorded.

Leucylglycyl-leucine ethyl ester,

$$C_4H_9\cdot CH(NH_2)\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH(C_4H_9)\cdot CO_2\cdot C_2H_5,$$

prepared by the action of leucylglycyl chloride hydrochloride on leucine ethyl ester, is a solid, which forms a crystalline *nitrate*, soften-

ing at about 147° (corr.), and melting and decomposing at about 160° (corr.). The free *tripeptide* is indefinite in crystalline form, and melts and decomposes at about 253° (corr.).

A new synthesis of leucyldiglycylglycine from leucyldiglycyl chloride hydrochloride and glycine ethyl ester is recorded.

A. McK.

Complex Compounds of Organic Imides. Succinimide Copper Derivatives. Leo Tschugaeff (*Ber.*, 1905, 38, 2899—2914. Compare Tschugaeff, Abstr., 1904, i, 478; Ley, this vol., ii, 524).—The compounds of the type $(Su)_2Cu,2a$, where Su represents the succinimide group, $C_6H_4(CO)_2N$, and a the particular amine used, are prepared by four general methods. (1) The reaction, formerly employed, where cupric chloride (1 mol.) and succinimide (2 mols.) are acted on by the amine in alcoholic solution is of general applicability, but has the objection that half of the amine used is lost, since the reaction proceeds in the sense $2SuH + CuCl_2 + 4a = Cu(Su)_2,2a + 2a,HCl$. (2) When copper turnings are brought into contact with an alcoholic solution of ammonia or of a primary amine in presence of oxygen, the copper is oxidised only slowly; when, however, succinimide is added, the solution quickly becomes dark blue, and a red compound separates at once. The change is represented by the equation $4SuH + 4a + 2Cu + O_2 = 2(Su)_2Cu,2a + 2H_2O$. (3) A suitable method where the amount of amine available is small is that of warming coppersuccinimide hexahydrate with the amine in alcoholic solution. (4) A solution of cuprammine hydroxide in water or in aqueous alcohol is first prepared, and then succinimide and an excess of alcohol added, the action proceeding according to the equation $Cu(2a)(OH)_2 + 2SuH = (Su)_2Cu,2a + 2H_2O$. This method, however, on account of the small yields obtained, is only of theoretical interest.

Diamminecoppersuccinimide, $(Su)_2Cu,2NH_3$, prepared by the oxidation method, begins to decompose in a closed capillary tube at 180°, and melts and decomposes at about 193°. Its aqueous solution has an ammoniacal odour; dilute solutions quickly assume a green tint and become turbid owing to hydrolysis. *Monoammine-triaquo-coppersuccinimide*, $(Su)_2Cu(NH_3),3H_2O$, prepared by allowing a solution of the diammine compound in a little water to evaporate in a partial vacuum over sulphuric acid, melts at about 130° when heated in a closed capillary tube. Alcoholic ammonia converts it into the diammine compound; it may also be formed by allowing the latter to remain in the air at the ordinary temperature for some time.

Dimethylaminecoppersuccinimide, $(Su)_2Cu,2NH_2Me$, prepared by the oxidation method, separates from alcohol in red needles and melts and decomposes at 168°. Its aqueous solution is dark blue, has an odour of methylamine, and when concentrated over sulphuric acid forms the *compound* $(Su)_2Cu(NH_2Me),3H_2O$; the latter is bluish-violet and melts at about 118°.

Diethylaminediaquocoppersuccinimide, $(Su)_2Cu,2NH_2Et,2H_2O$, is red and melts at 156°. Its aqueous solutions undergo marked hydrolysis with the formation of coppersuccinimide hexahydrate, $(Su)_2Cu,6H_2O$; the latter forms blue plates and cannot readily be re-

crystallised from water owing to the formation of basic coppersuccinimide derivatives. Coppersuccinimide hexahydrate gradually effloresces; it undergoes a delicate colour change with benzyl-, allyl-, or *iso*butyl-amine, a red compound being formed. Diethylamino-diaquocoppersuccinimide, in contradistinction to the corresponding ammonia and methylamine derivatives, can be preserved in a damp atmosphere without undergoing change.

The following *compounds* were prepared:

$(Su)_2Cu,2NH_2Pr^a$ (m. p. 167°); $(Su)_2Cu,2NH_2{\cdot}C_4H_9$, *n*- (m. p. 166°); *iso*- (m. p. 171°); *sec*-; *tert*.- (m. p. 161°); $(Su)_2Cu,2NH_2{\cdot}C_5H_{11}$ (*iso*-) (m. p. 171°); $(Su)_2Cu,2NH_2{\cdot}C_6H_{13}$ (*n*-) (m. p. 161°); $(Su)_2Cu,2NH_2{\cdot}C_3H_5$ (m. p. 172°); $(Su)_2Cu,2NH_2{\cdot}CH_2Ph$ (m. p. 181°); the *camphylamine* compound, $(Su)_2Cu,2NH_2{\cdot}CH_2{\cdot}C_9H_{15}$.

The tendency for secondary amines to form these diammine compounds is not so marked as that of the primary amines.

Bisdimethylaminediaquocoppersuccinimide, $(Su)_2Cu,2NHMe_2,2H_2O$, best prepared by the oxidation method, forms dark brownish-red, tetragonal prisms and melts at 133°. Its aqueous solutions are bluish-green and readily undergo hydrolytic dissociation.

Aliphatic tertiary amines do not form compounds with copper succinimide.

Dipyridinecoppersuccinimide, $(Su)_2Cu,2C_5NH_5$, forms brownish-red crystals which melt and decompose at about 175°. When its blue aqueous solution is slowly evaporated over sulphuric acid, it forms the *compound* $(Su)_2Cu,C_5NH_5,H_2O$, which crystallises in bluish-violet needles or prisms. When the solution of the latter compound in water is allowed to evaporate over sulphuric acid or when the dipyridine compound is treated with much water and then allowed to evaporate, coppersuccinimide hexahydrate separates.

The constitution of the compounds described is discussed.

A. McK.

Selenocyanopropionic Acid. M. Simon (*Monatsh.*, 1905, **26**, 959—970. Compare Hofmann, Abstr., 1889, 726).—*Potassium α-selenocyanopropionate*, $C_4H_4O_2NSeK$, is formed by the action of potassium selenocyanate (Muthmann and Schröder, Abstr., 1900, i, 479) on potassium α-chloropropionate in slightly warm, aqueous solution; it forms deliquescent, yellow or brown crystals, and is easily soluble in alcohol or water, but almost insoluble in benzene or chloroform. The *sodium* salt, $C_4H_4O_2NSeNa$, prepared from sodium selenocyanide and α-chloropropionate, forms small, slightly yellow crystals, is readily soluble in water, but less so in alcohol, and is only slightly hygroscopic.

Sodium selenocyanate, CNSeNa, formed by fusing sodium cyanide with selenium, crystallises from alcohol in white leaflets.

Ethyl α-selenocyanopropionate, $C_6H_9O_2NSe$, formed by boiling ethyl α-chloropropionate with potassium selenocyanate in alcoholic solution in a reflux apparatus, is obtained as a reddish-brown oil, which has an unpleasant odour and a burning taste, is soluble in ether, and has a sp. gr. >1. It is hydrolysed by boiling alcoholic sodium hydroxide with formation of sodium lactate, sodium selenocyanate and alcohol. The

methyl ester, formed by warming the potassium salt with methyl iodide, resembles the ethyl ester.

α-Selenocyanopropionic acid, $CNSe\cdot CHMe\cdot CO_2H$, liberated from its sodium salt by means of dilute sulphuric acid, forms a yellow, viscid liquid which has a characteristic odour, does not solidify at $-15°$, and has a strong acid reaction; when in contact with a small amount of water, it slowly evolves hydrogen cyanide, and yields on filter paper, after some time, a red selenium stain. In neutral solution, α-selenocyanopropionic acid forms with silver nitrate a white precipitate which becomes yellow and probably consists of a mixture of silver selenocyanate and lactate. Attempts to form a copper salt resulted also in decomposition of the acid. G. Y.

Action of Diazomethane on Ethylene and Diallyl. E. Azzarello (*Atti R. Accad. Lincei*, 1905, [v], **14**, ii, 285—286. Compare von Pechmann, Abstr., 1895, i, 328).—On passing dry ethylene through a well-cooled ethereal solution of diazomethane, pyrazoline is formed.

The action of diallyl on an ethereal solution of diazomethane yields a small proportion of an oil which has an alkaline reaction, boils at 70—80° under 28 mm. pressure, and gives a yellow precipitate with platinic chloride. T. H. P.

Decompositions of Ethanemercarbide with Alkali Sulphites and Sulphur Chloride. Karl A. Hofmann and H. Feigel (*Ber.*, 1905, **38**, 3654—3659. Compare Abstr., 1898, i, 635; 1900, i, 383). —When the chloride, $C_2Hg_6Cl_6$, is shaken with ten times its weight of a 10 per cent. benzene solution of sulphur chloride, no change occurs; it is also undecomposed when heated with sulphur chloride at 120°. The corresponding base, $C_2Hg_6O_4H_2$, on the other hand, when shaken with the benzene solution, yields yellow crystals of the *compound* $C_2Hg_4Cl_4S_2$, probably $\begin{matrix} C(HgCl)_2\cdot C(HgCl)_2 \\ | \qquad\qquad\quad | \\ S \text{———} S \end{matrix}$, the chlorine of which is readily precipitated as silver chloride.

When the chloride, $C_2Hg_6Cl_6$, is mixed with potassium polysulphide solution and the solution repeatedly renewed so long as mercuric chloride is formed, the *compound* $C_2Hg_4Cl_2SH_2$ is obtained in the form of brilliant yellow needles. The same product is obtained when the mixture is heated at 100° and is purified by washing with potassium sulphide solution, water, alcohol, carbon disulphide, and ether. When the yellow crystals are boiled with hydrochloric acid, an intense alliaceous odour is noticed, and a white, crystalline powder is formed which turns yellow on the addition of hot sodium hydroxide solution. The chlorine atoms are removed by silver nitrate and are thus presumably attached to mercury, and the formula $\begin{matrix} ClHg\cdot CH\cdot Hg \\ | \\ ClHg\cdot CH\cdot Hg \end{matrix}\!\!>\!S$ is suggested.

The base $C_2Hg_6O_4H_2$, when left for several weeks in contact with a methyl-alcoholic solution of ammonium polysulphide, which is repeatedly renewed, yields a yellow compound, which, after washing with potassium sulphide solution, has the composition $C_2Hg_6S_2O_2H_2$.

It has not been found possible to remove all the metal from these mercury compounds by means of sulphides and polysulphides. Tetramercuriethane cyanide reacts with potassium polysulphide yielding the *compound*, $C_4Hg_4SH_6$, probably $(Hg\colon CH\cdot CH_2\cdot Hg)_2S$. With a methyl-alcoholic solution of ammonium polysulphide, it yields $C_2Hg_2SH_4$. J. J. S.

Grignard's Reaction with Dihaloids. II. Felix B. Ahrens and Adolf Stapler (*Ber.*, 1905, **38**, 3259—3267. Compare this vol., i, 423).—The compound formed by the action of magnesium on ethylene dibromide in ethereal solution has the constitution

$$OBrEt_2\cdot Mg\cdot CH_2\cdot CH_2Br,$$

and its additive compound with benzaldehyde,

$$OBrEt_2\cdot CHPh\cdot O\cdot Mg\cdot CH_2\cdot CH_2Br\ ;$$

when treated with water under cooling, this is decomposed with formation of ether and benzaldehyde. The *additive* compound with *p*-tolualdehyde, $OBrEt_2\cdot CH(C_7H_7)\cdot O\cdot Mg\cdot CH_2\cdot CH_2Br$, is obtained as a white powder melting at 117°. The *additive* compound with piperonal, $OBrEt_2\cdot CH(C_6H_3\colon O_2\colon CH_2)\cdot O\cdot Mg\cdot CH_2\cdot CH_2Br$, melts at 210°.

The action of anhydrous bromine on magnesium in cooled ethereal solution leads to the formation of the *additive* compound, $OBrEt_2\cdot MgBr$, which is obtained as an unstable oil; in ethereal solution, it forms the following additive compounds having the constitution

$$OBrEt_2\cdot R\cdot O\cdot MgBr.$$

With benzaldehyde, $R = CHPh\colon$, a white, crystalline powder which melts partially at 164—165°; with *p*-tolualdehyde, $R = CH\cdot C_7H_7$: a white powder which commences to sinter at 105—107° and melts at 120—122°; with furfuraldehyde, $R = CH\cdot C_4H_3O$: a brown compound which commences to sinter and decompose at 164°; with ethyl acetoacetate, $R = C(OEt)\cdot CH_2\cdot COMe$: white leaflets, melting at 146—148°; with ethyl malonate, $R = C(OEt)\cdot CH_2\cdot CO_2Et$: a white powder which sinters at 124° and melts at 128—129°; with 2 : 6-dimethylpyridine, $R = NC_5H_3Me_2$: a white compound which commences to soften at 161°, and melts slowly at 168—230°; with piperidine, $R = NC_5H_{11}$: a yellowish-white substance which does not melt at 270°; with *p*-toluidine, $R = NH_2\cdot C_7H_7$: a white substance which sinters and blackens at 225°; with acetone, a deliquescent, yellow mass.

The action of iodine on magnesium in ethereal solution leads to the formation of the unstable *additive* compound, $OIEt_2\cdot MgI$; this is obtained as a viscid oil which slowly deposits crystals of magnesium iodide.

The action of bromine on calcium in cooled ethereal solution leads to the formation of the *additive* compound, $OBrEt_2\cdot CaBr$, which is obtained as a yellowish-brown, crystalline mass containing unchanged calcium particles; it forms with piperidine in ethereal solution a white, powdery *additive* derivative. G. Y.

Modern Position of the Benzene Theory. Hugo Kauffmann (*Chem. Centr.*, 1905, ii, 965; from *Chem. Zeitschr.*, 4, 289—290).—The paper contains a description of the principles on which research on the constitution of benzene has been developed in recent times.

E. W. W.

Derivatives of *cyclo*Hexane. Léon Brunel (*Ann. Chim. Phys.*, 1905, [viii], 6, 200—288).—The present paper is mainly a *résumé* of work already published (compare Abstr., 1903, i, 157, 338, 680, 695; this vol., i, 123, 268, 274, 340), and contains in addition a description of the following new compounds: o-*Iodo*cyclo*hexyl benzoate*, $C_6H_{10}I\cdot CO_2Ph$, crystallises from a mixture of alcohol and ether in large, colourless plates melting at 54°. o-*Bromoiodo*cyclo*hexane*, $C_6H_{10}BrI$, a pale red oil with an odour similar to that of camphor, is insoluble in water, soluble in alcohol, ether, or acetic acid, has a sp. gr. 2·07 at 0°, and boils at 134—136° under 28 mm. pressure (compare Abstr., 1903, i, 157). o-*Ethylamino*cyclo*hexanol*, $OH\cdot C_6H_{10}\cdot NHEt$, crystallises in small, colourless, hygroscopic needles which become coloured by the action of light, melt at 44—45°, and boil at 222° under atmospheric pressure; its *hydrochloride* forms colourless, deliquescent plates melting at 155°. *Ethyl dihydroxy*cyclo*hexylamine*, $NEt(C_6H_{10}\cdot OH)_2$, crystallises in small, colourless, odourless plates melting at 114°, and boiling at 352°; its *hydrochloride* forms colourless crystals melting at 162—163°. o-*Diethylamino*cyclo*hexanol*, $OH\cdot C_6H_{10}\cdot NEt_2$, is a colourless oil boiling at 230° and forming a crystalline *hydrochloride* melting at 168°. o-*Phenylamino*cyclo*hexanol*, $OH\cdot C_6H_{10}\cdot NHPh$, is a colourless, crystalline substance melting at 58°, boiling at 210° under 46 mm. or 327° under atmospheric pressure; its *hydrochloride* melts at 150—151°. o-*Phenylmethylamino*cyclo*hexanol*, $OH\cdot C_6H_{10}\cdot NMePh$, is a colourless oil boiling at 192° under 28—30 mm., or 202° under 40 mm., or at 329° under 767 mm. pressure (compare Abstr., 1903, i, 680). *Methoxy*-Δ^2-cyclo*hexene*, $C_6H_9\cdot OMe$, a colourless mobile oil with a strong alliaceous odour, boils at 139·8° and has a sp. gr. 0·928 at 0°; ethoxy-Δ^2-*cyclo*hexene, $C_6H_9\cdot OEt$, a colourless, mobile oil boiling at 154·5° and having a sp. gr. 0·911 at 0° (compare Crossley, Trans., 1904, 85, 1415—1416); the cyclo*hexenol*, $C_6H_9\cdot OH$, obtained from either of the two preceding compounds, is a liquid boiling at 164—166° and reacting with phenylcarbimide to form the urethane, $C_6H_9\cdot O\cdot CO\colon NPh$, melting at 108°. M. A. W.

Double Salts of Iodoxy-derivatives with Mercuric Chloride and Bromide. Luigi Mascarelli (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 199—205).—The double salts here described may be prepared by the following methods: (1) by adding mercuric chloride or bromide to a hot aqueous solution of the iodoxy-compound; (2) by treating phenyl iododichloride with mercuric chloride in aqueous solution; (3) in the case of iodoxybenzene, by passing a current of dry chlorine into a solution of iodobenzene in glacial acetic acid containing yellow mercuric oxide. These double salts all crystallise well and are more stable towards the action of heat than the iodoxy-derivatives they contain.

The following compounds have been prepared: $C_6H_5O_2I,HgCl_2$, which crystallises from water in white needles, decomposing without deflagrating at 225—227°; $C_6H_5O_2I,HgBr_2$, which separates from water in radiating masses of white needles, beginning to colour at about 260°, and becoming quite yellow at 305°. *p*-Iodoxytoluene

yields: (1) $C_6H_4MeO_2I,HgCl_2$, which crystallises from water in thin, plate-like masses of white needles, decomposing at 214—215° when rapidly heated, and (2) a *mercuribromide*, forming silky, mammillary masses of slender, white needles, which blacken at about 290°. *m*-Iodoxytoluene gives: (1) $C_6H_4MeO_2I,HgCl_2$ which separates in radiating white prisms, turning yellow at about 200° and decomposing at 260°; (2) a *mercuribromide*, which crystallises in slender needles beginning to turn yellow at 240°. *o*-Iodoxytoluene forms:

$$(1)\ C_6H_4MeO_2I,\tfrac{1}{2}HgCl_2,$$

which separates in stellar aggregates of white needles, blackening at 190° and decomposing rapidly at 210°; (2) $C_6H_4MeO_2I,\frac{1}{2}HgBr_2$, which forms flocculent masses of slender prisms turning yellow at 240°.

The following iodoxy-derivatives have been prepared: *β-iodoxynaphthalene*, $C_{10}H_7IO_2$, exploding at 200°; p-*chloroiodoxybenzene*,

$$C_6H_4Cl\cdot IO_2,$$

exploding at 232°; p-*bromoiodoxybenzene*, $C_6H_4Br\cdot IO_2$, exploding at 231°, and p-*nitroiodoxybenzene*, $NO_2\cdot C_6H_4\cdot IO_2$, exploding at 216°. Unsuccessful attempts have been made to prepare double salts of mercuric haloids with these compounds, some of the latter being insoluble in water and other solvents, whilst others crystallise unchanged in presence of mercuric salts.

p-Nitrotoluene forms the *double salt*, $NO_2\cdot C_6H_4Me,HgCl_2$, separating from alcohol in pale yellow, acicular crystals, which soften at about 105°, begin to melt at 150°, and blacken at about 222°.

T. H. P.

Action of Alkyl Haloids on the Sodium Derivatives of Arylsulphoneacetonitriles. JULIUS TRÖGER and PAUL VASTERLING (*J. pr. Chem.*, 1905, [ii], 72, 323—340. Compare Tröger and Hille, this vol., i, 336; Tröger and Volkmer, this vol., i, 356).—Arylsulphonedialkylacetonitriles are prepared by heating the disodium derivatives, formed by the action of sodium ethoxide in absolute alcoholic solution on arylsulphonacetonitriles, with methyl iodide, ethyl or propyl bromides, or benzyl chloride in sealed tubes or in a reflux apparatus on the water-bath. They are more stable than the parent substances, hydrolysis, as also formation of amidoximes, taking place only with difficulty or not at all.

Benzenesulphonediethylacetonitrile, $SO_2Ph\cdot CEt_2\cdot CN$, crystallises from alcohol in colourless, rhombic plates and melts at 78°. *Benzenesulphonedibenzylacetonitrile*, $SO_2Ph\cdot C(C_7H_7)_2\cdot CN$, crystallises from alcohol in long, glistening, sparingly soluble needles and melts at 157—157·5°. *Benzenesulphonedi*iso*propylacetonitrile* is obtained as a viscid, brown oil.

p-*Chlorobenzenesulphonediethylacetonitrile*, $C_6H_4Cl\cdot SO_2\cdot CEt_2\cdot CN$, separates from alcohol in small crystals and melts at 81°. p-*Chlorobenzenesulphonedipropylacetonitrile* and p-*chlorobenzenesulphonedi*iso*propylacetonitrile* are obtained as oils. p-*Chlorobenzenesulphonedibenzylacetonitrile* crystallises from hot alcohol and melts at 125°.

p-*Bromobenzenesulphonediethylacetonitrile* separates from alcohol in small, white, rhombic crystals and melts at 94°. p-*Bromobenzene-*

sulphonedibenzylacetonitrile crystallises from alcohol in white needles and melts at 145°.

p-*Iodobenzenesulphonedibenzylacetonitrile* crystallises from alcohol in small needles or glistening spangles and melts at 166°.

α-*Naphthalenesulphonedimethylacetonitrile* crystallises from alcohol in white spangles and melts at 115°. α-*Naphthalenesulphonedibenzylacetonitrile* separates from alcohol in small, white, rhombic crystals and melts at 180°.

β-*Naphthalenesulphonedimethylacetonitrile* crystallises from alcohol in glistening, white spangles and melts at 115°.

β-*Naphthalenesulphonediethylacetonitrile* is obtained as a viscid, brown oil. β-*Naphthalenesulphonedibenzylacetonitrile* crystallises in small, white, sparingly soluble needles and melts at 177°.

The action of 1 mol. of benzyl chloride on the monosodium derivative of β-naphthalenesulphoneacetonitrile leads to the formation of the dibenzyl derivative, together with a *substance* which crystallises in light, white needles, melts at 128°, and may be the monobenzyl-derivative.

ψ-*Cumylsulphonediethylacetonitrile* is obtained as an oil.

p-*Phenetolesulphondiethylacetonitrile* separates from alcohol in small, white, rhombic crystals and melts at 81°. p-*Phenetolesulphonedibenzylacetonitrile* crystallises in small, white needles and melts at 119°.

o-*Anisolesulphonediethylacetonitrile* is obtained as an oil. o-*Anisolesulphonedibenzylacetonitrile* forms small, rhombic crystals and melts at 123°.

p-*Anisolesulphonedibenzylacetonitrile* separates from alcohol in small, rhombic crystals and melts at 119°.

Sodio-p-*chlorobenzenesulphoneacetonitrile*, $C_6H_4Cl \cdot SO_2 \cdot CHNa \cdot CN$, is obtained as a hygroscopic, dirty-white powder when the nitrile is treated with 1 mol. of sodium ethoxide in alcoholic solution and the product precipitated by ether; when warmed with 1 mol. of benzyl chloride in ethereal alcoholic solution, it yields a small amount of a crystalline *product* melting at 117°. The *monosodium* derivative of *p*-bromobenzenesulphoneacetonitrile, obtained in the same manner, forms a hygroscopic, yellowish-white powder, and when heated with 1 mol. of benzyl chloride in ethereal alcoholic solution yields a *substance* which forms small, yellow crystals and melts at 104°.

Whilst benzenesulphoneacetonitrile and α-naphthalenesulphoneacetonitrile are hydrolysed by hydrogen chloride in glacial acetic acid solution in a sealed tube on the water-bath, with formation of benzenesulphoneacetic and α-naphthalenesulphoneacetic acids respectively, and *p*-bromobenzenesulphoneacetonitrile is hydrolysed to the acid by prolonged heating with aqueous sodium hydroxide, β-naphthalenesulphonedimethylacetonitrile is hydrolysed only partially by concentrated sulphuric acid in a sealed tube at 120—150° for one day, or by prolonged heating with 15 per cent. alcoholic potassium hydroxide, with formation of a small amount of β-*naphthalenesulphonedimethylacetic acid*, which was identified by means of its *barium* salt.

Benzenesulphonedipropylthioacetamide, $SO_2Ph \cdot CPr_2 \cdot CS \cdot NH_2$, is formed when the nitrile is heated with alcoholic ammonium sulphide

in a sealed tube in the water-bath; it is obtained as a yellow, voluminous substance.

p-*Anisolesulphonedibenzylthioacetamide*, formed in the same manner, is obtained in small, yellowish-white, loose crystals and melts at 114°. G. Y.

p-Dichloroaminobenzene [2:5-Dichloroaniline]. EMILIO NOELTING and ÉMILE KOPP (*Ber.*, 1905, 38, 3506—3515).—2:5-Dichloroaniline melts at 50° and boils at 246° (corr.) at 744 mm. pressure; it is a weak base, the salts of which can be crystallised from alcohol, but are decomposed by water. The *hydrochloride* forms colourless needles and melts at 191—192°; the *sulphate*, glistening scales melting at 196—197°; the *nitrate*, scales which char at 165°, liberating brown vapour. The *benzoyl* derivative crystallises from alcohol in silky needles and melts at 120°. The *thiocarbamide*, $CS(NH\cdot C_6H_3Cl_2)_2$, prepared with some difficulty, crystallises from alcohol in very slender, colourless needles and melts at 174°; it yields a thiocarbimide when heated with strong mineral acids.

When diazotised, 2:5-dichloroaniline shows a great tendency to form a diazoamino-compound, and to prevent this it is necessary to use at least 7—8 mols. of acid; the best method is to diazotise in concentrated sulphuric acid. The *diazoperbromide*, $C_6H_3Cl_2N_2Br_3$, precipitated by ether from a solution in acetone, forms small, yellow plates and melts and decomposes at 160°. 2:5-*Dichlorobenzeneazo-β-naphthol*, $C_6H_3Cl_2\cdot N_2\cdot C_{10}H_6\cdot OH$, separates from acetic acid in slender, orange-red needles and melts at 184°; condensation products were also obtained with salicylic acid, β-naphtholdisulphonic acids R and G, and aminonaphtholdisulphonic acid H.

2:5-*Dichlorobenzonitrile*, $C_6H_3Cl_2\cdot CN$, forms colourless, silky needles, melts at 130°, sublimes when cautiously heated, and is saponified by heating with fuming hydrochloric acid at 180°.

1:4-*Dichloro-2-bromobenzene* forms glistening, white needles and melts at 35°.

2:5-*Dichlorophenol* forms a colourless, radially-crystalline mass, melts at 58°, and boils at 211° under 744 mm. pressure.

2:5-*Dichlorophenylhydrazine*, $C_6H_2Cl_2\cdot N_2H_3$, crystallises in slender, white needles from hot water, in which it is fairly soluble, melts at 105°, becomes yellow on exposure to the air, and reduces cold Fehling's solution. The hydrochloride crystallises from dilute hydrochloric acid in white needles. The p-*nitrobenzylidene* derivative,

$$C_6H_3Cl_2\cdot NH\cdot N\!:\!CH\cdot C_6H_4\cdot NO_2,$$

crystallises in orange-coloured needles and melts at 220°. The p-*dimethylaminobenzylidene* derivative forms yellow, stout crystals and melts at 120°. The *osazone* with dihydroxytartaric acid is readily prepared, and passes, when heated on the water-bath, into the *pyrazolone*, $C_6H_3Cl_2\cdot N\!<\!\begin{array}{l}CO\cdot \underset{|}{C}\cdot N\cdot NH\cdot C_6H_3Cl_2\\ N{=\!=}C\cdot CO_2H\end{array}$, which crystallises (unacetylated) from acetic anhydride in slender, orange-coloured needles and melts and decomposes at 236°.

The *sodium nitrosoamino*-compound (*iso*diazotate), $C_6H_3Cl_2N_2ONa$,

separates from alcohol in long, yellow crystals and yields a sparingly soluble white *iso*diazohydroxide.

The *monosulphonic acid*, $C_6H_2Cl_2(NH_2)\cdot SO_3H$ [2 : 5 : 4 : 1], separates from hot water in anhydrous, white, glistening needles. The *sodium* salt separates in white, glistening plates with $5H_2O$, and the *barium* salt is anhydrous. The acid is oxidised by chromic acid to 2 : 5-dichloroquinone, and is converted by bromine into 2 : 5-*dichloro*-4 : 6-*dibromoaniline*, $C_6HCl_2Br_2\cdot NH_2$, which is insoluble in water and in dilute mineral acids, separates from 50 per cent. acetic acid in white needles, and melts at 108°. The sulphonic acid yields a stable *diazonium-anhydride* which separates in glistening, white needles. 2 : 5-*Dichlorophenylhydrazinesulphonic acid*, $C_6H_2Cl_2(N_2H_3)\cdot SO_3H$, forms anhydrous, slender, white needles and yields a canary-yellow tartrazine; the *sodium* salt separates with $3\frac{1}{2}H_2O$ in white scales with a fatty lustre.

The *diacetyl* derivative of dichloro-*p*-phenylenediamine melts at 294—296°. The o-*diamine* sublimes in glistening, white needles, which melt at 100° and do not become coloured when kept; *phenanthradichlorophenazine*, $C_6H_2Cl_2<\begin{matrix}N:C\cdot C_6H_4\\ \vert \quad \vert \\ N:C\cdot C_6H_4\end{matrix}$, forms soft, yellow needles and melts at 289°. T. M. L.

Nitration of Amines. ANGELO ANGELI and GIUSEPPE MARAGLIANO (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 127—132).—The water which is eliminated in the reaction between a nitric ester and hydroxylamine is formed from an oxygen atom of the nitro-group and the hydrogen of the amino-residue. This is shown by the fact that the reaction takes place even in absence of the hydroxyl of the hydroxylamine. Thus, the addition of sodium to an absolute ethereal solution of molecular proportions of aniline and acetyl nitrate leads to the formation of the sodium salt of phenylnitroamic acid, $NPh:NO\cdot OH$, which represents the tautomeric form of phenylnitroamine, $NHPh\cdot NO_2$. The latter is isomeric with nitrosophenylhydroxylamine, to which may be ascribed the two forms

$$OH\cdot NPh\cdot NO \rightleftarrows Ph\cdot NO:NOH.$$

Hence, although nitrosophenylhydroxylamine can be obtained by the action (1) of hydroxylamine on nitrobenzene, (2) of hyponitrous acid on nitrosobenzene, or (3) of nitrous acid on phenylhydroxylamine, it is impossible to prepare it by the interaction of nitric acid and aniline. T. H. P.

Action of Magnesium Alkyl Haloids on Amines and on Ammonium, Amine, and Hydrazine Salts, and a New Method of Formation of Hydrocarbons. JOSEF HOUBEN (*Ber.*, 1905, 38, 3017—3021. Compare Abstr., 1904, i, 1014; Sachs and Sachs, Abstr., 1904, i, 925).—The action of 1 mol. of aniline on 2 mols. of magnesium methyl iodide in ethereal solution cooled by ice leads to the formation of the additive *compound*, $NHPh\cdot MgI,MgMeI$, which does not absorb carbon dioxide, but reacts with 1 mol. of aniline to form methane and the *compound* $NHPh\cdot MgI$; this forms an *additive compound*, $NHPh\cdot CO_2\cdot MgI$, with carbon dioxide in ethereal solution cooled with ice.

Ammonium chloride, bromide, iodide, carbonate, sulphate, nitrate, persulphate and chromate, phenylhydrazine hydrochloride, and aniline hydrochloride and nitrate are decomposed by magnesium methyl iodide, with formation of methane and in most cases of a heavy, colourless oil, insoluble in ether; the similar reaction takes place more violently with magnesium ethyl chloride or bromide; magnesium phenyl bromide and magnesium benzyl chloride are decomposed by ammonium chloride. At higher temperatures, as, for example, in boiling anisole solution, a second hydrogen atom of the ammonium, amine, or hydrazine salt is substituted, and a smaller quantity of the salt is therefore required for the decomposition of the same amount of the magnesium alkyl haloid. G. Y.

Behaviour of Hydrogen Cyanide towards Phenylcarbimide. WALTER DIECKMANN and HEINRICH KÄMMERER (*Ber.*, 1905, **38**, 2977—2986. Compare Dieckmann, Hoppe, and Stein, this vol., i, 135).—Hydrogen cyanide and phenylcarbimide interact only in the presence of alkaline substances, such as potassium cyanide, sodium carbonate, sodium acetate, or pyridine. *Cyanoformanilide*, NHPh·CO·CN, is formed by adding a few drops of pyridine to a solution of hydrogen cyanide and phenylcarbimide in benzene; it crystallises from benzene in glistening, colourless leaflets or from aqueous alcohol or acetic acid in fan-like aggregates of broad needles, melts and decomposes into its generators at about 120°, is readily soluble in alcohol, ether, chloroform, or carbon disulphide, but less so in benzene or glacial acetic acid, and is only sparingly soluble in light petroleum or water. It gives a violet-red coloration with potassium dichromate in concentrated sulphuric acid solution. By prolonged contact with water or aqueous solvents, more quickly when warmed, it is decomposed with formation of hydrogen cyanide and diphenylcarbamide, and when boiled with alcohol for twelve hours, it yields hydrogen cyanide and ethyl phenylcarbamate. The alkaline solution of cyanoformanilide deposits diphenylcarbamide slowly at the ordinary temperature, more quickly when heated, the solution containing the alkali cyanide together with small amounts of oxanilic acid; in alcoholic potassium hydroxide or sodium ethoxide, ethyl phenylcarbamate appears instead of the diphenylcarbamide. With aqueous ammonia, it forms phenylcarbamide, with aniline, diphenylcarbamide, and with phenylhydrazine, diphenylsemicarbazide.

The action of cyanoformanilide on ethyl sodioacetoacetate leads to the formation of ethyl acetomalonanilate, melting at 57°. Phenyloxamide is formed by the action of hydrogen chloride on cyanoformanilide in glacial acetic acid solution cooled by ice, or by the action of hydrogen peroxide on cyanoformanilide in presence of an alkali hydroxide. With hydrogen sulphide in alcoholic solution, cyanoformanilide yields phenylthionoxamide melting at 176° (Reissert, Abstr., 1904, i, 991).

In aqueous solution, in presence of traces of an alkali hydroxide, potassium cyanide, sodium carbonate or acetate, or pyridine, hydrogen cyanide and phenylcarbimide interact with development of heat to form a *product*, which may be diphenylallophanonitrile,

NHPh·CO·NPh·CO·CN,

or diphenylparabanimide, $CO<\begin{matrix}NPh\cdot CO\\ NPh\cdot C:NH\end{matrix}$; it crystallises from alcohol in white needles, melts at 137°, is easily soluble in glacial acetic acid, but only sparingly so in cold alcohol, ether, benzene, or carbon disulphide, and is almost insoluble in water. It dissolves in dilute alkali hydroxides, and is gradually decomposed into diphenylcarbamide, oxanilic acid, and a small quantity of alkali cyanide; with alcoholic alkali hydroxides, ethyl phenylcarbamate is formed, whilst with ammonia, aniline, and phenylhydrazine it yields phenylcarbamide, diphenylcarbamide, and diphenylsemicarbazide respectively. When treated with acids, it yields diphenylparabanic acid. G. Y

Action of Phosphorus Pentachloride on Tartranil. SADAJIRO OKADA (*Mem. Coll. Sci. Eng. Kyōto*, 1904—1905, 1, 168—171).—Dichloromaleinanil and 2 : 3 : 4 : 5-tetrachloro-1-phenylpyrrole are formed when *d*-tartranil is treated with phosphorus pentachloride. Dichlorosuccinanil is assumed to be the first product in the formation of dichloromaleinanil, but it immediately loses 1 mol. of hydrogen chloride with the formation of monochloromaleinanil, in which one atom of hydrogen is then replaced by chlorine. H. M. D.

Simple Preparation of Pure Ethylaniline from Commercial Ethylaniline. G. BLUME and H. KLÖFFLER (*Ber.*, 1905, 38, 3276).—Pure ethylaniline hydrochloride is obtained in a yield of 80 per cent. of the theoretical by adding 65 c.c. of concentrated hydrochloric acid to 97 grams of commercial ethylaniline, and completing the precipitation by passing a current of hydrogen chloride through the filtrate. G. Y.

Optically Active α-Phenylethylamines (α-Aminoethylbenzenes). JOHAN M. LOVÉN (*J. pr. Chem.*, 1905, [ii], 72, 307—314. Compare Abstr., 1897, i, 37; Pope and Harvey, Trans., 1899, 75, 1110; Kipping and Hunter, Trans., 1903, 83, 1147; Marckwald and Meth, this vol., i, 272).—When α-phenylethylamine and *l*-malic acid are stirred together with water, solution takes place with development of heat, and *α-phenylethylamine* l-*malate* separates as a crystalline powder; this crystallises in large, three-sided prisms, is soluble in 18·1 parts of water at 10°, and yields the *d*-base having $[\alpha]_D$ +40·27° at 15°. l-*α-Phenylethylamine* l-*malate* is highly soluble in water, crystallising only from a viscid syrup.

The base obtained from the filtrate from the *l*-malate of the *d*-base yields, when treated with *d*-tartaric acid in a small quantity of water, l-*α-phenylethylamine hydrogen* d-*tartrate*, which crystallises in hemimorphic, monoclinic, short prisms or stout plates, or, on rapid cooling of the hot saturated aqueous solution, in slender needles containing water of crystallisation; the hydrated form changes into the stable, anhydrous modification when warmed or on addition of a trace of the prismatic crystals. The *l*-base has $[\alpha]_D$ −39·72° at 6°; its *carbamide*, crystallises in matted, slender needles and has $[\alpha]_D$ −43·6° with a concentration of 0·1406 gram/c.c., or −52·1° with a concentration of

0·03717 gram/c.c.; the *nitrate*, $CHMePh\cdot NH\cdot CO\cdot NH_2,HNO_3$, crystallises in glistening plates. G. Y.

Palladium. ALEXANDER GUTBIER [with A. KRELL and R. L. JANSSEN] (*Zeit. anorg. Chem.*, 1905, **47**, 23—41).—In former papers (this vol., ii, 584), the preparation of double salts and palladosammine derivatives by interaction of palladous chloride and bromide with the hydrochlorides and hydrobromides of aniline and *o*- and *p*-toluidine has been described. Corresponding compounds of xylidine, *p*-anisidine, and α- and β-naphthylamine have now been prepared by the methods previously given. Whereas the double salts can be readily crystallised from dilute hydrochloric and hydrobromic acids respectively, the palladosammine derivatives are extremely insoluble, and so far no satisfactory solvent has been found for the naphthylamine and benzidine compounds. The xylidine and *p*-anisidine derivatives can be crystallised from a large excess of alcohol.

The phenylenediamines react differently from the other bases, since salts of the meta- and para-compounds yield double salts with the palladous salts under all conditions, whereas the ortho-compounds yield only platosammine derivatives. The latter are so stable that they can be recrystallised from the corresponding dilute halogen acids.

All the palladosammine compounds here described are acted on by warm concentrated ammonia, the base being set free and a pallado-diammine chloride or bromide, $[Pd(NH_3)_4Cl_2]$, formed. On heating, the base is driven off and finally the diammine loses two molecules of ammonia, palladosammine chloride or bromide remaining in solution.

Xylidine palladous chloride, $(C_6H_3Me_2\cdot NH_3Cl)_2,PdCl_2$, is obtained in clear, brown needles; the *bromide* forms reddish-brown leaflets. p-*Anisidine palladous chloride*, $[C_6H_4(OMe)\cdot NH_3Cl]_2,PdCl_2$, crystallises in yellowish-brown leaflets; the bromide also forms lustrous, yellowish-brown leaflets. α-*Naphthylamine palladous chloride*,

$$(C_{10}H_7\cdot NH_3Cl)_2,PdCl_2,$$

occurs in glistening, yellowish-brown leaflets, the *bromide* in dark brownish-red needles. The *chloride* of the β-compound forms yellowish-red leaflets; the corresponding *bromide* crystallises in dark reddish-brown leaflets. *Benzidine palladous chloride*,

$$C_{12}H_8(NH_3Cl)_2,PdCl_2,$$

crystallises in brown leaflets, the bromide in small, reddish-brown leaflets. m-*Phenylenediamine palladous chloride*, $C_6H_4(NH_3Cl)_2,PdCl_2$, crystallises in glancing copper-coloured leaflets, the corresponding para-compound in small, reddish-brown leaflets; its *bromide* also occurs in reddish-brown leaflets.

Dixylylpalladosammine chloride, $Pd(C_6H_3Me_2\cdot NH_2)_2Cl_2$, crystallises from hot alcohol in small, golden-yellow needles; the *bromide* separates in small, glistening, golden-yellow needles. *Di*-p-*anisidyl-palladosammine chloride*, $Pd[C_6H_4(OMe)NH_2]_2Cl_2$, and the corresponding *bromide* both crystallise from hot alcohol in small, yellow needles. *Di-α-naphthylpalladosammine chloride* and *bromide* and the corresponding β-compounds are all obtained as very slightly soluble, yellow powders. *Benzidylpalladosammine chloride*, $Pd[C_6H_4\cdot NH_2]_2Cl_2$,

cannot easily be obtained pure on account of the great difficulty of separating it from the slightly soluble benzidine hydrochloride; it forms a yellow precipitate. The *bromide* is also very difficult to purify; it forms a yellowish-brown precipitate. o-*Phenylene palladosammine chloride*, $Pd[C_6H_4(NH_2)_2]Cl_2$, crystallises from dilute hydrochloric acid in small, greenish-yellow, shining needles; the *bromide* separates from dilute hydrobromic acid in golden-brown, glancing needles. G. S.

Attempts to Synthesise Mezcaline. ARTHUR HEFFTER and R. CAPELLMANN (*Ber.*, 1905, **38**, 3634—3640. Compare Abstr., 1901, i, 737).—3 : 4 : 5-Trimethoxybenzylmethylamine,

$$C_6H_2(OMe)_3 \cdot CH_2 \cdot NHMe,$$

has been synthesised, and it is shown that it is not identical, but isomeric with mezcaline.

Gallonitrile trimethyl ether, $C_6H_2(OMe)_3 \cdot CN$, may be obtained by Krüss' method (Abstr., 1884, 1314) by heating gallic acid trimethyl ether with lead thiocyanate. It crystallises from dilute alcohol in needles, melts at 95°, and dissolves readily in alcohol or ether, but only sparingly in hot water. Its solution in concentrated sulphuric acid has a yellowish-red colour. When reduced with sodium by Ladenburg's method, it yields a considerable amount of the corresponding acid and hydrogen cyanide, but very little primary amine.

Gallaldehyde trimethyl ether, $C_6H_2(OMe)_3 \cdot CHO$, may be prepared by the oxidation of the corresponding alcohol (Abstr., 1891, 1218) by the action of potassium cyanide in a mixture of alcohol and sodium carbonate on hexamethoxybenzil or by the oxidation of hexamethoxyhydrobenzoin with potassium dichromate and acetic acid.

Hexamethoxybenzil monoxime,

$$C_6H_2(OMe)_3 \cdot C(:N \cdot OH) \cdot CO \cdot C_6H_2(OMe)_3,$$

exists in two modifications. The α-compound, which is insoluble in benzene, crystallises from dilute alcohol in long needles melting at 158°. The β-derivative is soluble in benzene, crystallises from dilute alcohol in slender, felted needles, and melts at 138°.

Hexamethoxyhydrobenzoin,

$$C_6H_2(OMe)_3 \cdot CH(OH) \cdot CH(OH) \cdot C_6H_2(OMe)_3,$$

obtained as a by-product in the reduction of gallamide trimethyl ether, crystallises from alcohol in well-developed needles melting at 215°. Its solution in concentrated sulphuric acid has a yellow colour. The *diacetate* melts at 190°.

Gallaldehyde trimethyl ether, purified by means of its bisulphite compound, crystallises from dilute alcohol in glistening plates, melts at 77°, and is readily soluble in alcohol or ether. The *oxime* crystallises in long needles, melts at 91°, and yields a crystalline *hydrochloride*. When reduced with sodium amalgam and alcohol, the oxime yields 3 : 4 : 5-*trimethoxybenzylamine*, $C_6H_2(OMe)_3 \cdot CH_2 \cdot NH_2$, in the form of a yellow oil with pronounced alkaline properties and is readily soluble in water, alcohol, or ether. The *sulphate*, $(C_{10}H_{15}O_3N_2)_2,H_2SO_4,3H_2O$, crystallises from water in absolute glistening needles and is insoluble in alcohol. The *platinichloride* crystallises in yellow needles and melts at 197°.

Trimethoxybenzyltrimethylammonium iodide,

$C_6H_2(OMe)_3 \cdot CH_2 \cdot NMe_3I$,

crystallises from water in stout plates melting at 218° and readily soluble in water or alcohol. The *platinichloride* melts at 215° and is sparingly soluble in water. This quaternary ammonium iodide is not identical, but isomeric with methylmezcaline methiodide. J. J. S.

Resolution of Phenylbenzylmethylpropylammonium Bases into their Optical Antipodes. EDGAR WEDEKIND and EMANUEL FRÖHLICH (*Ber.*, 1905, **38**, 3438—3446).—*Phenylbenzylmethylpropylammonium iodide*, prepared either from methylpropylaniline and benzyl iodide or from benzylmethylaniline and propyl iodide, crystallises in colourless, flat, six-sided plates, which become yellow at 140° and melt and decompose at 147°. *Phenylbenzylmethylpropylammonium bromide*, prepared from methylpropylaniline and benzyl bromide, crystallises in colourless prisms and decomposes at 173—174°. Benzyl chloride and methylpropylaniline do not interact. *Phenylbenzylmethylpropylammonium* d-*camphorsulphonate* crystallises in rhombic plates, often a centimetre long, and melts at 179°; when fractionally crystallised from methyl formate, a fraction was obtained, the base from which gave $[\alpha]_D$ +13·28° and $[M]_D$ +62·55°, and, converted into the corresponding iodide, had $[\alpha]_D$ +3·21° and $[M]_D$ +11·8°.

l-*Phenylbenzylmethylpropylammonium* d-*bromocamphorsulphonate*, prepared by the interaction of the ammonium bromide with the sulphonic acid, yields a first fraction, about half the theoretical amount, having $[\alpha]_D$ +4·83° and $[M]_D$ +26·59°. After two crystallisations from a mixture of ethyl acetate and alcohol, it shows $[\alpha]_D$ −2·67° and $[M]_D$ −14·67°. The corresponding l-*phenylbenzylmethylpropylammonium iodide* has in alcoholic solution $[\alpha]_D$ −96·47° and $[M]_D$ −354°, and in chloroform solution $[\alpha]_D$ −102° and $[M]_D$ −374°. The chloroform solution showed autoracemisation, the rotation falling in one case in four hours to $[M]_D$ −178°, whilst next day the solution was optically inactive. The *l*-iodide decomposes at 149—150°.

The d-*phenylbenzylmethylpropylammonium iodide*, obtained from the mother liquors of the bromocamphorsulphonate, has $[\alpha]_D$ +86·74°, $[M]_D$ +319°. E. F. A.

Introduction of Iodine into Tolylcarbamides. PAUL ARTMANN (*Monatsh.*, 1905, **26**, 1091—1108).—*5-Iodotolyl-2-carbamide*,

$C_7H_6I \cdot NH \cdot CO \cdot NH_2$,

is formed by the action of potassium iodide and iodate on *o*-tolylcarbamide in boiling aqueous solution and treatment of the solution with hydrochloric acid, or by heating *o*-tolylcarbamide with iodine and mercuric oxide in alcoholic solution at 70—75°, or by treating 5-iodo-2-aminotoluene with potassium cyanate in cold glacial acetic acid solution. It crystallises from aqueous alcohol in long, white, hair-like needles, is easily soluble in alcohol, pyridine, or glacial acetic acid, less so in boiling water, and is insoluble in ether, benzene, or light petroleum; when boiled with acetic anhydride in a reflux apparatus, it is decomposed with formation of 5-iodo-2-acetotoluidide. The *acetyl* derivative, $C_{10}H_8O_2N_2I$, is formed by dropping acetyl chloride

into the pyridine solution of 5-iodotolyl-2-carbamide at 0°; it crystallises in small, white prisms and melts at 234—235°. 6-*Iodotolyl*-3-*carbamide* can be prepared from *m*-tolylcarbamide or from 6-iodo-3-aminotoluene by the same three methods as 5-iodotolyl-2-carbamide. It crystallises in short, white needles, melts at 187°, and when boiled with acetic anhydride forms 6-iodo-3-acetotoluidide. The *acetyl* derivative, formed by the action of acetyl chloride on 6-iodotolyl-3-carbamide in pyridine solution, crystallises in sheaves of slender, white needles and melts at 170—171°. 3-*Iodo*-6-*nitrotoluene*, $C_7H_6O_2NI$, is formed by the action of potassium iodide on diazotised 6-nitro-3-aminotoluene; it crystallises in slender, orange needles, melts at 84°, is volatile in a current of steam, and is reduced by ferrous sulphate and ammonia in aqueous solution at 66—70° to 5-*iodo*-2-*aminotoluene*, C_7H_8NI. This crystallises in long, white needles, melts at 91—92°, and is easily soluble in alcohol, ether, glacial acetic acid, benzene, light petroleum, or hot water. The salts are hydrolysed by water and decompose slowly on exposure to the air; the *hydrochloride*, C_7H_8NI,HCl, forms short, white needles; the *nitrate*, C_7H_8NI,HNO_3, crystallises in slender, tetragonal scales. 5-*Iodo*-2-*acetotoluidide*, $C_9H_{10}ONI$, formed by the action of acetic anhydride on 5-iodo-2-aminotoluene in ethereal solution, crystallises from alcohol in matted, slender needles and melts at 161—162°.

6-*Iodo*-3-*aminotoluene*, formed by reduction of 6-iodo-3-nitrotoluene, crystallises in colourless leaflets, melts at 98—99°, and decomposes slowly on exposure to air. The *hydrochloride* forms short needles, the *nitrate* crystallises in tree-like aggregates of slender needles. 6-*Iodo*-3-*acetotoluidide*, formed by boiling 6-iodo-3-toluidine with acetic anhydride, crystallises in white needles and melts at 132°. G. Y.

Action of Nitric Acid on the Halogen Derivatives of *p*-Alkylphenols. II. Action of Nitric Acid on the Bromo-derivatives of *p*-Cresol. THEODOR ZINCKE (*Annalen*, 1905, **341**, 309—354).—[With WILHELM EMMERICH.]—5-*Bromo*-3-*nitro*-p-*cresol*, $NO_2 \cdot C_6H_2BrMe \cdot OH$, is prepared by the action of nitric acid on bromo-*p*-cresol in acetic acid solution, or by the action of nitrous acid on an acetic acid solution of either monobromo- or dibromo-*p*-cresol, and crystallises in yellow needles melting at 68°. It dissolves in dilute sodium carbonate solution with a red coloration, and is oxidised by nitric acid to bromonitro-*p*-toluquinone. 5 : 6-*Dibromo*-3-*nitro*-p-*cresol* (?), prepared by the action of nitrous acid on an acetic acid solution of tribromo-*p*-cresol, crystallises in yellow, shining needles or leaflets melting at 124° and yields a red sodium salt. When heated with nitric acid, dibromonitro-*p*-toluquinone is formed. 2 : 5 : 6-*Tribromo*-3-*nitro*-p-*cresol* is prepared in a similar manner from tetrabromo-*p*-cresol, or more easily from tetrabromoquinnitrole, and crystallises in pale yellow needles melting at 160°; the *sodium* salt is intensely red. *Bromonitro*-p-*toluquinone*, $CO{<}{\begin{smallmatrix}CH:C(NO_2)\\CMe{=\!=}CBr\end{smallmatrix}}{>}CO$ or $CO{<}{\begin{smallmatrix}CMe:C(NO_2)\\CH{=\!=\!=}CBr\end{smallmatrix}}{>}CO$, prepared from monobromo-*p*-cresol or bromonitro-*p*-cresol by oxidation with nitric acid, crystallises in golden needles or six-sided plates,

melting at 135—136°, and yields a derivative with aniline which crystallises in brownish-red leaflets, decomposing at 220—230°. *Bromonitro-p-toluquinol*, prepared by reducing the quinone with hydriodic acid in acetic acid solution, crystallises in long, yellow needles melting at 175—176°; its salts are of a dark red colour, but its *diacetyl* derivative, $NO_2 \cdot C_6HBrMe(OAc)_2$, crystallises in colourless prisms melting at 118°. 5-*Bromo-3-amino-p-toluquinol*, prepared by reduction of the bromonitrotoluquinone with tin and hydrochloric acid, crystallises in needles which melt and decompose at 148—149°; it is readily oxidised in alkaline solution, and forms a hydrochloride which crystallises in colourless needles; it is oxidised by ferric chloride to a *compound*, $C_7H_6O_2NBr$, probably an iminoquinone, which crystallises in black needles, dissolves in sulphuric acid with a blue coloration, and is decomposed with evolution of ammonia by alkali hydroxides. The *triacetyl* derivative of the bromoaminotoluquinol, $NHAc \cdot C_6HBrMe(OAc)_2$, crystallises in needles melting at 203—204°.

Dibromonitro-p-toluquinone, $CO<\begin{matrix}CBr{=}CBr\\CMe{:}C(NO_2)\end{matrix}>CO$, prepared by the oxidation of nitrodibromo-*p*-cresol, crystallises in golden leaflets melting at 165° and decomposing at 175—180°; it is reduced by hydriodic acid in acetic acid to a *quinol* which crystallises in needles melting at 157—158°.

[With M. Buff.]—Di-, tri-, and tetra-bromo-*p*-cresols are very readily converted into quinnitroles, which in their turn yield ψ-quinols. On reduction, both quinnitroles and ψ-quinols yield the same phenols. In many respects the bromoquinnitroles behave differently to the chloroquinnitroles. The ψ-quinols react with Grignard's reagent, yielding di-ψ-quinols, which are converted by sulphuric acid into hydrocarbons having a quinonoid structure.

2 : 3 : 5 : 6-*Tetrabromomethylquinnitrole*, $NO_2 \cdot CMe<\begin{matrix}CBr{:}CBr\\CBr{:}CBr\end{matrix}>CO$, prepared by the action of concentrated nitric acid on tetrabromo-*p*-cresol in acetic acid solution, crystallises in white plates melting and decomposing at 100°; it passes easily into the corresponding ψ-quinol, and when heated with alcoholic hydrochloric acid yields 2 : 5 : 6-tribromo-3-nitro-*p*-cresol. 2 : 3 : 5 : 6-*Tetrabromomethyl-ψ-quinol*,

$$OH \cdot CMe<\begin{matrix}CBr{:}CBr\\CBr{:}CBr\end{matrix}>CO,$$

prepared either from the corresponding quinnitrole or by the action of nitric acid on tetrabromo-*p*-cresol, crystallises in monoclinic plates melting at 205°; its *acetyl* derivative forms colourless needles melting at 175—176°. 2 : 3 : 5-*Tribromo-6-hydroxymethylquinol*,

$$OH \cdot CMe<\begin{matrix}C(OH){:}CBr\\CBr{=}CBr\end{matrix}>CO,$$

prepared by the action of 10 per cent. sodium hydroxide on the corresponding ψ-quinol, crystallises with H_2O in monoclinic plates which melt and decompose at 131°, and when anhydrous melt at 152°. Its *monoacetyl* derivative crystallises in needles melting at 179°. Tetrabromo-ψ-toluquinol yields an *anilide*, $OH \cdot CMe<\begin{matrix}C(NHPh){:}CBr\\CBr{=}CBr\end{matrix}>CO$, which crystallises in yellow needles melting at 206°; its *acetyl*

derivative forms greenish-yellow needles which are sensitive to light and decompose at 170—190°. *Octabromodiphenolmethane*,

$$OH\cdot C_6Br_4\cdot CH_2\cdot C_6Br_4\cdot OH,$$

prepared by warming the ψ-quinol with concentrated sulphuric acid, crystallises in white needles, melting and decomposing at 280—281°. When the quinol and bromine are heated under pressure at 100°, *tetrabromo*-p-*cresol ψ-bromide* is formed.

3 : 6-*Dichloro*-2 : 5-*dibromomethyl-ψ-quinol*, $C_6Br_2Cl_2OMe(OH)$, prepared by heating tetrabromotolu-ψ-quinol with alcoholic hydrochloric acid under pressure at 100°, crystallises in white plates or prisms melting at 172°, and is soluble in alkali hydroxides. Its *acetyl* derivative crystallises in needles melting at 147°. It reacts with aniline with elimination of hydrogen chloride and the formation of an *anilide*, $C_{13}H_{10}O_2NClBr_2$, which crystallises in yellow needles melting at 197°.

3 : 6-*Dichloro-5-bromo-2-hydroxy-ψ-toluquinol*, $C_7H_5O_3Cl_2Br,2H_2O$, prepared by the action of 10 per cent. sodium hydroxide on dichlorodibromo-ψ-quinol, crystallises in colourless plates melting at 174—175°; dibromodichloro-ψ-quinol is reduced by stannous chloride in acetic acid solution to 3 : 6-*dichloro*-2 : 5-*dibromo*-p-*cresol*, which crystallises in long needles melting at 175—176°; its *acetyl* derivative crystallises in needles melting at 146—147°. When heated with excess of bromine under pressure at 100°, it is converted into 3 : 6-*dichloro*-2 : 5-*dibromo*-p-*cresol-ψ-bromide*, which forms colourless needles melting at 166°. Boiling water converts the ψ-bromide into a *hydroxybenzyl alcohol*, which crystallises in needles melting and decomposing at 175°; the corresponding *methoxy*-derivative, $OMe\cdot C_6Cl_2Br_2\cdot CH_2\cdot OH$, is obtained when the ψ-bromide is boiled with methyl alcohol, and crystallises in plates melting at 155°. 3 : 6-*Dichloro*-2 : 5-*dibromotoluquinnitrole*, $C_7H_3O_3NCl_2Br_2$, is prepared by the action of nitric acid on dichlorodibromo-*p*-cresol, and crystallises in needles melting and decomposing at 83—85°; when boiled with methyl alcohol, it yields the methoxy-derivative just mentioned.

2 : 3 : 5-*Tribromoquinnitrole*, $NO_2\cdot CMe\lessgtr\begin{matrix}CH:CBr\\CBr:CBr\end{matrix}\gtrless CO$, prepared by the action of nitric acid on tribromo-*p*-cresol, could not be prepared in a pure state, but the corresponding 2 : 3 : 5-*tribromomethyl-ψ-quinol* is obtained when the tribromo-*p*-cresol is treated with nitric acid in acetic acid solution; it forms plate-like crystals melting at 128°; its *acetyl* derivative crystallises in plates melting at 127—128°. On reduction with stannous chloride, the tribromo-*p*-cresol is regenerated; when heated with sulphuric acid, the ψ-quinol yields *hexabromodiphenolmethane*, which crystallises in needles melting at 202—203°.

Chlorodibromomethyl-ψ-quinol is prepared from dichlorodibromotoluquinol and crystallises in prisms melting at 134—135°; its *acetyl* derivative crystallises in needles melting at 117°. On reduction, the ψ-quinol yields *chlorodibromo*-p-*cresol*, which crystallises in needles melting at 65°; its *acetyl* derivative melts at 76°.

Dibromo-*p*-cresol yields with nitric acid 2 : 6-*dibromomethylquinnitrole*, crystallising in needles melting and decomposing at 62° (compare Auwers, Abstr., 1902, i, 217). It is converted into dibromomethyl-ψ-quinol,

$OH\cdot CMe<\begin{smallmatrix}CH:CBr\\CH:CBr\end{smallmatrix}>CO$, when suspended in a solution of nitric acid in acetic acid; it crystallises in needles melting at 134—135°. When treated with concentrated sulphuric acid, it forms *tetrabromodiphenolmethane*, $CH_2(C_6H_2Br_2\cdot OH)_2$, melting at 227°.

Tetrabromomethylethyldi-ψ-quinol, $OH\cdot CMe<\begin{smallmatrix}CBr:CBr\\CBr:CBr\end{smallmatrix}>CEt\cdot OH$, prepared after Grignard's method from tetrabromomethyl-ψ-quinol by treatment with magnesium foil and ethyl iodide in ethereal solution, crystallises in white needles melting at 190—191° and soluble in alkali hydroxides; when heated with hydrogen bromide in acetic acid solution, it yields the *compound* $C_9H_7Br_5$, which crystallises in needles melting at 169—170° and is insoluble in alkali hydroxides. *Tetrabromodiethyl-ψ-quinol*, $OH\cdot CEt<\begin{smallmatrix}CBr:CBr\\CBr:CBr\end{smallmatrix}>CEt\cdot OH$, prepared in a similar manner from tetrabromoethylquinol, crystallises in plates melting at 179—180°, and is converted by hydrogen bromide in acetic acid solution into a *compound* (possibly *tetrabromo*-p-*diethylbenzene*), melting at 112—114°. *Dichlorodibromomethylethyldi-ψ-quinol*, $C_9H_{10}O_2Cl_2Br_2$, is prepared in similar manner and crystallises in needles melting at 183°. K. J. P. O.

Action of Nitric Acid on Tri- and Tetra-bromo-*p*-ethylphenols. THEODOR ZINCKE and HANS REINBACH (*Annalen*, 1905, **341**, 355—364).—The bromo-derivatives of *p*-ethylphenol resemble those of *p*-cresol in their behaviour towards nitric acid; quinnitroles have not, however, been obtained, although they are probably formed as intermediate products; the ψ-quinols were isolated.

2 : 5-*Dibromo-3-nitro*-p-*ethylphenol*, $C_6HBr_2Et(OH)\cdot NO_2$, prepared from 2 : 3 : 5-tribromo-*p*-ethylphenol by the action of nitric acid or sodium nitrite on its acetic acid solution, crystallises in yellow needles melting at 105—106° and forms a red sodium salt. The *acetyl* derivative crystallises in pale yellow prisms melting at 60°. *Tribromonitro*-p-*ethylphenol*, prepared in a similar manner from tetrabromo-*p*-ethylphenol, crystallises in yellow needles melting at 122—123°; its *acetyl* derivative forms yellow plates melting at 113°.

2 : 3 : 5-*Tribromoethyl-ψ-quinol*, $OH\cdot CEt<\begin{smallmatrix}CH=CBr\\CBr:CBr\end{smallmatrix}>CO$, prepared by prolonged treatment of tribromo-*p*-ethylphenol with nitric acid in acetic acid solution, crystallises in needles melting at 105° and soluble in alkali hydroxide; it yields an *acetyl* derivative and regenerates the phenol on reduction. 2 : 3 : 5 : 6-*Tetrabromoethyl-ψ-quinol*, prepared from tetrabromoethylphenol by boiling with nitric acid containing nitrous acid, crystallises in needles melting at 139—140°. Its *acetyl* derivative forms crystals melting at 124°. *Tribromoethyl*-p-*quinone*,

$$CO<\begin{smallmatrix}CEt:CBr\\CBr:CBr\end{smallmatrix}>CO,$$

prepared by the action of concentrated sulphuric acid on finely-powdered tetrabromo-ψ-quinol, crystallises in yellow leaflets or needles melting at 118—120°. With aniline, it gives an *anilide*, $O:C_6Br_2Et(NHPh):O$, crystallising in dark violet needles melting

and decomposing at 167—170°. *Tribromoethylquinol*, $C_6Br_3Et(OH)_2$, prepared by reducing the quinone with stannous chloride, crystallises in needles melting at 141°. Its *diacetyl* derivative crystallises in prisms or plates melting at 156—157°. K. J. P. O.

Some Phenolic Ethers containing the ψ-Allyl Chain R·CMe:CH₂. AUGUSTE BÉHAL and MARC TIFFENEAU (*Compt. rend.*, 1905, **141**, 596—597. Compare Abstr., 1904, i, 742).—Phenolic ethers containing the ψ-allyl chain are completely hydrogenated by the action of sodium and absolute alcohol, forming the corresponding *iso*propyl compound; *o*-, *m*-, and *p*-*iso*propylanisoles, boiling respectively at 194—196°, 205—208°, and 210—212°, were thus prepared from the corresponding ψ-propenylanisoles. *p*-*iso*Propylphenetole, boiling at 220° and having a sp. gr. 0·946 at 0°, was prepared in similar manner from ψ-propenylphenetole; 1-*iso*propyl-3 : 4-veratrole, boiling at 232—236°, from 1-ψ-propenyl-3 : 4-veratrole, and 1-*iso*propyl-3 : 4-catechol methylene ether, boiling at 230—233°, from 1-ψ-propenyl-3 : 4-catechol methylene ether (compare Delange, Abstr., 1904, i, 741). By the action of potassium permanganate, the ψ-allyl compounds are oxidised, yielding derivatives of acetophenone; *o*-methoxyacetophenone, boiling at 245°, *m*-methoxyacetophenone, boiling at 132° under 15 mm. pressure, and *p*-methoxyacetophenone, melting at 38°, were obtained from the three corresponding ψ-propenylanisoles, 3 : 4-dimethoxyacetophenone, melting at 48°, from 1-ψ-propenyl-3 : 4-veratrole, and 3 : 4-methylenedioxyacetophenone, melting at 88°, from 1-ψ-propenyl-3 : 4-catechol methylene ether. The iodohydrins of the ψ-allyl compounds suffer an intermolecular rearrangement under the action of silver nitrate or mercuric oxide (compare Abstr., 1901, i, 272; 1902, i, 666), whereby *p*-ψ-propenylanisole is converted into *p*-methoxybenzyl methyl ketone (compare Tardy, Abstr., 1903, i, 46), *p*-ψ-propenylphenetole into *p*-ethoxybenzyl methyl ketone, 1-ψ-propenyl-3 : 4-catechol methylene ether into methylene-3 : 4-dioxyacetophenone, and 1-ψ-propenyl-3 : 4-veratrole into 3 : 4-dimethoxybenzyl methyl ketone (compare Wallach, Abstr., 1904, i, 753, and Höring, this vol., i, 593). By the action of potassium hydroxide, the iodohydrins of the ψ-allyl compounds are converted into the corresponding substituted ethylene oxide, which on distillation yields the corresponding hydratropaldehyde (compare this vol., i, 523, 591; Bougault, Abstr., 1902, i, 452). M. A. W.

Phenols Insoluble in Aqueous Alkali Hydroxides. MOISSEI ROGOFF (*J. pr. Chem.*, 1905, [ii], 72, 315—322. Compare Abstr., 1901, i, 152; Fosse, Abstr., 1902, i, 304; 1903, i, 510; 1904, i, 83, 336, 337; Fosse and Robyn, this vol., i, 607).—A *résumé* is given of the phenols which have been described as insoluble in aqueous alkali hydroxides. The author agrees with Fosse and Robyn (*loc. cit.*) that the insolubility of the dinaphthaxanthyl phenols is due to the quadrivalency of the oxygen atom, a view which is supported by the isolation of xanthoxonium salts (Werner, Abstr., 1902, i, 50). The insolubility of the phenols of the acridine series is due similarly to the quinquevalent nitrogen atom.

The condensation products of aldehydes with β-naphthylamine and

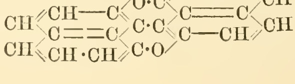
with β-naphthol, described in the present paper, are insoluble in cold, and only sparingly soluble in warm, dilute alkali hydroxides.

The *product* obtained on heating 1 mol. of *p*-hydroxybenzaldehyde with 2 mols. of β-naphthylamine in alcoholic hydrochloric acid solution in a sealed tube at 150—155° crystallises from dilute acetic acid in matted needles, melts at 249—251° (corr.), and is easily soluble in methyl or ethyl alcohol or acetone, forming solutions with bluish-violet fluorescence. The *benzoate* crystallises in needles and melts at 268·5—269·5° (corr.); the *acetate* crystallises from hot dilute alcohol and melts at 204—207° (corr.).

The *condensation product* from vanillin and β-naphthylamine crystallises from chloroform in slender needles, melts at 254—256° (corr.), forms solutions with slight bluish-violet fluorescence in methyl or ethyl alcohol, ether, acetone, or benzene, and is soluble in aqueous-alcoholic sodium hydroxide.

p-Hydroxyphenylnaphthaxanthen (Fosse, Abstr., 1904, i, 83) is formed when *p*-hydroxybenzaldehyde is heated with β-naphthol in glacial acetic acid solution in a sealed tube at 190—200°; it melts at 203—205° (corr.) (207°, Fosse). The *acetyl* derivative melts at 190—192·5° (corr.); the *benzoyl* derivative crystallises in needles and melts at 273·5—274·5° (corr.). When condensed in presence of hydrogen chloride in glacial acetic acid solution, *p*-hydroxybenzaldehyde and β-naphthol form *p*-hydroxyphenylnaphthaxanthen, together with a substance which crystallises from alcohol, melts at 267·5° (corr.), is insoluble in aqueous alkali hydroxides, but dissolves in aqueous-alcoholic sodium hydroxide, and when warmed with sulphuric acid has a green fluorescence.

The condensation of *m*-hydroxybenzaldehyde and β-naphthol in glacial acetic acid solution at 190—200° leads to the formation of a compound which crystallises from dilute methyl alcohol in needles, melts at 249—251° (corr.), is almost insoluble in boiling aqueous alkali hydroxides, and dissolves in warm concentrated sulphuric acid to form a solution which has a green fluorescence. G. Y.

Oxidation of ββ-Dinaphthol. HANS BÜNZLY and HERMAN DECKER (*Ber.*, 1905, **38**, 3268—3273).—When oxidised with potassium ferricyanide in alkaline solution, ββ-dinaphthol yields (*a*) *o*-β-hydroxynaphthoylbenzoic acid (Walder, Abstr., 1883, 666), which crystallises from boiling glacial acetic acid in matted, colourless scales, melts at 255°, and sublimes, forming yellow drops of oil; these crystallise on cooling in yellow needles melting at 145—150°; (*b*) a neutral *substance*, $C_{20}H_{12}O_3$, which remains after removal of the acid from the oxidation product; it crystallises from carbon disulphide in dark brown needles, melts at 230°, is sparingly soluble in glacial acetic acid, alcohol, or ether, and dissolves in concentrated sulphuric acid to form a green solution which has a blue fluorescence and becomes blue when heated. When heated, it evolves vapours with a quinone-like odour, and forms a small quantity of a *substance*, which may be dinaphthylene dioxide,  ; it sublimes

in long, slender, golden needles, melts at 245°, is only sparingly soluble in organic solvents, forming solutions with dark blue fluorescence, and dissolves in concentrated sulphuric acid to form a red solution, which becomes violet-red and finally blue on dilution with water. On reduction with hydriodic acid and phosphorus under pressure, it yields a small quantity of partially reduced naphthalene derivative, and when distilled with zinc dust it is converted to a small extent into naphthalene.

The *picrate* crystallises in large, black needles and decomposes into its generators when treated with solvents. The *tetranitro*-derivative, $C_{20}H_6O_{10}N_4$, is formed by the action of nitric acid of sp. gr. 1·5 on the dioxide; on addition of alcohol to its solution in nitrobenzene, it separates as a cinnabar-like, crystalline meal, does not melt at 300°, is sparingly soluble in most organic solvents, but somewhat more soluble in glacial acetic acid or nitrobenzene, and forms a light red solution in concentrated sulphuric acid.

The action of methyl sulphate on 2 : 7-dihydroxynaphthalene in aqueous sodium hydroxide solution leads to the formation of the mono- and di-methyl ethers. 7-Hydroxy-2-methoxynaphthalene, $C_{11}H_{10}O_2$, crystallises from water in white scales, or from alcohol in long needles, melts at 113—114°, is soluble in aqueous alkali hydroxides, sublimes without decomposition, is volatile in a current of steam, has only a slight fruity odour, and dissolves in concentrated sulphuric acid to form a dark yellow solution with bluish-green fluorescence, from which it is precipitated unchanged on dilution with water. 2 : 7-Dihydroxynaphthalene and its mono- and di-methyl ethers give with aqueous ferric chloride white or yellow precipitates which rapidly become black. G. Y.

Dinaphthylene Oxides. OSKAR ECKSTEIN (*Ber.*, 1905, **38**, 3660—3663).—The dinaphthylene oxides obtained by heating β-naphthol with litharge (Knecht and Unzeitig, Abstr., 1881, 281) and by heating β-dinaphthol with zinc chloride or phosphorus pentachloride (*Ber.*, 1882, **15**, 2171) are shown to be identical and to have the constitution 1 : 1′-dinaphthyl 2 : 2′ oxide. Both melt at 158·5° (corr.) and both yield a monopicrate melting at 163—163·5° (corr.) and a dipicrate melting at 168·5°. J. J. S.

γ-Substituted Anthracene Derivatives. ALFRED GUYOT and CH. STAEHLING (*Bull. Soc. chim.*, 1905, [iii], **33**, 1104—1121. Compare Haller and Guyot, Abstr., 1904, i, 314, 659, and this vol., i, 188).—9 : 10-*Dihydroxy*-9 : 10-*diphenyl*-2-*methyldihydroanthracene*,

$$C_6H_4<\begin{matrix}CPh(OH)\\CPh(OH)\end{matrix}>C_6H_3Me,$$

prepared by the action of magnesium phenyl bromide on 2-methylanthraquinone, forms small, colourless, apparently cubical crystals, melts at 240°, and is difficultly soluble in organic solvents, but dissolves in sulphuric acid forming an indigo-blue solution. The *dichloride*, obtained by the action of hydrogen chloride on the parent substance dissolved in benzene, forms colourless leaflets, melts at 148°,

and at the same time evolves hydrogen chloride; the latter is also produced when the dichloride is dissolved in sulphuric acid, an indigo-blue solution being formed. The *dimethyl ether*, formed in the usual manner, crystallises from its solution in benzene on addition of methyl alcohol and melts at 169°; the *diethyl ether*, similarly prepared, forms small, brilliant white crystals and melts at 183·5°.

9 : 10-Dihydroxy-9 : 10-diphenyl-2-methyldihydroanthracene acts, in presence of acids, as an oxidising agent and yields, under these conditions, 9 : 10-*diphenyl-2-methylanthracene*, which separates from benzene on addition of alcohol in greenish-yellow crystals, melts at 213°, and is slightly soluble in alcohol, ether, or acetic acid, but readily so in benzene or its homologues. The solutions show a fine bluish-violet fluorescence (compare Abstr., 1904, i, 314). On reduction by means of sodium amalgam in alcohol, this hydrocarbon is converted into the corresponding *dihydride*, which crystallises from acetic acid in colourless, silky needles, melts at 179°, and is soluble in most organic solvents. On exposure to air, the dihydride slowly acquires a greenish tint due to superficial oxidation to the parent hydrocarbon, and, like the latter, on oxidation with potassium dichromate yields the original 9 : 10-dihydroxy-9 : 10-diphenyl-2-methyldihydroanthracene. The latter readily condenses with various aromatic compounds to yield complex derivatives: thus, with dimethylaniline, it furnishes 9 : 10-*tetramethyldiaminodiphenyl*-9 : 10-*diphenyl-2-methyldihydroanthracene*, $C_6H_4{<}{\substack{CPh\cdot C_6H_4(NMe_2) \\ CPh\cdot C_6H_4(NMe_2)}}{>}C_6H_3Me$. This exists in two forms (*cis* and *trans*), both being colourless, crystalline powders: one melts at 312° and is slightly soluble in most organic solvents, the other melts at about 147° and is readily soluble. Both forms yield crystalline *picrates* and *platinichlorides* and *salts*, which are dissociated by water. These substances give no coloration when dissolved in sulphuric acid. When the condensation is carried out at 100°, only one of the hydroxyl groups is replaced by the dimethylaniline residue. The *product* appears to be a mixture of at least two isomerides and, on adding hydrochloric acid to its solution in alcohol, two substances are obtained, one melting at 155° and the other at 125°. These may be isomerides or may be related to each other as hydroxy-compound and ethyl ether.

9 : 10-*Dihydroxy*-9 : 10-*a-dinaphthyldihydroanthracene*, prepared by the action of magnesium a-naphthyl bromide on anthraquinone, forms small, colourless crystals containing 1 mol. of benzene, and is soluble in acetic acid, ether, or boiling toluene, but scarcely so in other solvents. When dissolved in boiling benzene and treated with hydrogen chloride, the corresponding dichloride is probably first formed, but this, under the conditions of the experiment, loses 1 mol. of hydrogen chloride and yields a *monochloro*-derivative, which forms greenish-yellow crystals, melts at 266°, and is readily soluble. The position of the chlorine atom in this substance is not known.

When reduced by zinc and acetic acid, the dihydroxy-compound yields 9 : 10-*di-a-naphthylanthracene*; this forms small, pale yellow crystals, and dissolves in benzene or its homologues with a pronounced violet fluorescence.

9 : 10-*Dihydroxy-9-phenyl-10-α-naphthyldihydroanthracene*,

$$C_6H_4<\begin{matrix}CPh(OH)\\C(C_{10}H_7)(OH)\end{matrix}>C_6H_4,$$

prepared by the action of magnesium naphthyl bromide on phenyloxanthranol, separates from solutions in benzene in small, apparently cubical crystals, melts at 220°, and has properties similar to those of the other dihydroxy-compounds of this type. The corresponding *dichloride* crystallises from benzene in small, colourless prisms containing 1 mol. of the solvent, which is rapidly lost at 15°; the effloresced product melts at 160°. The *dimethyl ether* forms small, brilliant crystals and melts at 230°; the *diethyl ether* resembles it and melts at 239°.

9-*Phenyl-10-α-naphthylanthracene*, prepared by reducing the parent substance with zinc and acetic acid, forms yellow, microscopic crystals, melts at about 229°, and is readily soluble in benzene and its homologues, much less so in alcohol or acetic acid; the solutions show a bluish-violet fluorescence. This substance, on reduction with sodium amalgam in alcohol, furnishes 9-*phenyl-10-α-naphthyldihydroanthracene*. This crystallises in colourless needles, but assumes a violet tint, on exposure to air, due to superficial oxidation and melts at about 225°.

9 : 10-*Tetramethyldi*-p-*aminodiphenyl-9-phenyl-10-α-naphthyldihydroanthracene*, produced by condensing dimethylaniline with dihydroxyphenylnaphthyldihydroanthracene dissolved in acetic acid, is a colourless, crystalline powder, melts at about 260°, and gives no coloration with sulphuric acid. T. A. H.

Condensation of ψ-Phenols with Phenols. KARL AUWERS and E. RIETZ (*Ber.*, 1905, 38, 3302—3307).—ψ-Phenols do not condense so readily with phenols as with tertiary aromatic amines (Abstr., 1904, i, 995). The mixture has to be heated for several hours at 100—150° in the absence of a solvent. The products are diphenylmethane derivatives, and as a rule pure products can only be isolated when the phenol has only one ortho-hydrogen or the para-hydrogen atom unsubstituted. In certain cases, 2 mols. of ψ-phenol react yielding bis-derivatives, which are more sparingly soluble.

3 : 5-Dibromo-4-hydroxybenzyl bromide (Abstr., 1903, i, 621) and *o*-cresol yield a product melting at 99—105° and consisting probably of a mixture of *o*- and *p*-dibromohydroxybenzylcresols.

With *p*-cresol, 3′ : 5′-*bis*-3 : 5-*dibromo-4-hydroxybenzyl*-p-*cresol*,

$$OH \cdot C_6H_2Br_2 \cdot CH_2 \cdot C_6H_2Me(OH) \cdot CH_2 \cdot C_6H_2Br_2 \cdot OH,$$

is obtained; it crystallises from benzene in colourless needles melting at 201—203°, and readily soluble in alcohol, ether, or acetic acid. The *tribenzoate*, $C_{42}H_{28}O_6Br_4$, crystallises from acetic acid in glistening needles, melts at 201—202°, and is insoluble in alkalis. When reduced with sodium and boiling alcohol, the tetrabromo-derivative yields *bis*-p-*hydroxybenzyl*-p-*cresol*, $C_6H_2Me(OH) \cdot (CH_2 \cdot C_6H_4 \cdot OH)_2$, melting at 212—214°. The *triacetate*, $C_{27}H_{26}O_6$, melts at 117—118°.

Dibromohydroxybenzyl-p-*cresol* (3 : 5-*dibromo*-4 : 2′-*dihydroxy*-5′-*methyldiphenylmethane*), $OH \cdot C_6H_2Br_2 \cdot CH_2 \cdot C_6H_3Me \cdot OH$, which is also obtained

from *p*-cresol, melts at 105—106·5° and is readily soluble in most organic solvents.

Bisdibromohydroxybenzyl-p-*xylenol*, $C_{22}H_{18}O_3Br_4$, obtained from the ψ-phenol and *p*-xylenol, melts at 205°, and the corresponding *mono*-derivative, $C_{15}H_{14}O_2Br_2$, at 153—155°.

Dibromohydroxybenzyl-ψ-cumenol, $C_{16}H_{16}O_2Br_2$, crystallises from a mixture of light petroleum and benzene in pale rose-coloured plates melting at 146°.

β-Naphthol yields the *mono*-derivative, $OH\cdot C_6H_2Br_2\cdot CH_2\cdot C_{10}H_6\cdot OH$, melting at 168—169°. The *diacetate* melts at 159—160°. J. J. S.

Action of Methyl Alcohol on Hexabromo-*o*-quinocatechol Ether. C. LORING JACKSON and PHILIP A. SHAFFER (*Amer. Chem. J.*, 1905, **34**, 460—467).—An improved method is described for the preparation of hexabromo-*o*-quinocatechol ether, first prepared by Jackson and Koch (Abstr., 1901, i, 597). When this compound is left in contact with methyl alcohol, a reaction takes place very slowly with formation of the additive *compound*, $C_{12}O_4Br_6,2MeOH$, which crystallises from alcohol in white, rhombic plates, melts and decomposes at 220—221°, and is soluble in benzene or acetone, soluble to the extent of 4·3 per cent. in boiling alcohol, and insoluble in water. This compound is best obtained by adding solution of sodium methoxide to the hexabromo-*o*-quinocatechol ether suspended in methyl alcohol and treating the product with hydrochloric or sulphuric acid; the *sodium* derivative, $C_{12}O_4Br_6,MeOH,MeONa$, is unstable, and on decomposition yields a *substance* which crystallises in red needles, decomposes at about 280°, and is soluble in water or alcohol. By the action of methyl alcohol and bromine on the methyl alcohol additive compound, a *substance* is formed which melts at about 150°. When phenylhydrazine is added slowly to a mixture of hexabromo-*o*-quinocatechol ether and nitrobenzene, hexabromodihydroxycatechol ether is produced; this reaction furnishes a convenient method for the preparation of this substance. E. G.

Action of Dilute Nitric Acid on Guaiacolsulphonic Acid. OTTO KÜHLING (*Ber.*, 1905, **38**, 3007—3008. Compare Armstrong, this Journal, 1871, **24**, 112).—When boiled with dilute nitric acid, potassium guaiacolsulphonate yields dinitroguaiacol, melting at 123—124° (Herzig, Abstr., 1883, 464), and *dinitrodihydroxydimethoxydiphenyl*, $OH\cdot C_6H_2(NO_2)(OMe)\cdot C_6H_2(NO_2)(OMe)\cdot OH$, which forms a yellow, crystalline powder, melts and decomposes at 283°, and dissolves in aqueous alkali hydroxides to form red solutions. G. Y.

Condensation of Pyrogallol with Acetone and with Methyl Ethyl Ketone. RUDOLF FABINYI and TIBOR SZEKI (*Ber.*, 1905, **38**, 3527—3531).—The *compound* $C_6(OH)_3 \begin{array}{c} \diagup CMe_2 \diagdown \\ \!-\!CMe_2\!-\! \\ \diagdown CMe_2 \diagup \end{array} C_6(OH)_3$, prepared by heating a mixture of pyrogallol, acetone, and acetic and hydrochloric acids in a sealed tube at 145° during three-quarters of an hour, crystallises from acetic acid in slender, brownish- or reddish-white crystals,

and melts and decomposes at 260—265°. The *hexa-acetyl* derivative, $C_{33}H_{36}O_{12}$, separates from methyl alcohol in colourless scales and melts without decomposition at 247—248°. The *hexabenzoyl* derivative, $C_{63}H_{48}O_{12}$, separates from a mixture of acetic acid, nitrobenzene, and alcohol in minute, colourless scales and melts at 289°. The *dibromo*-derivative, $C_{21}H_{22}O_6Br_2$, forms small, bluish-white needles and melts and decomposes at 197—200°. Its *hexa-acetyl* derivative, $C_{33}H_{34}O_{12}Br_2$, separates from alcohol or acetic acid in white, glistening scales and melts at 260°.

The *condensation product*, $C_{24}H_{30}O_6$, from pyrogallol and methyl ethyl ketone, crystallises from acetic acid and melts and decomposes at 260°. Its *hexa-acetyl* derivative crystallises from dilute acetic acid in slender, white needles and melts at 212°. T. M. L.

Decomposition of *m*- and *p*-Nitrobenzyl Alcohols under the Influence of Aqueous and of Alcoholic Sodium Hydroxide. Paul Carré (*Compt. rend.*, 1905, **141**, 594—596. Compare this vol., i, 307).—*m*- and *p*-Nitrobenzyl alcohols are decomposed less readily than the *o*-compound by the action of alkali hydroxides, and the products are less complex; *m*-nitrobenzyl alcohol, when heated at 100° with aqueous 10 per cent. sodium hydroxide, yields *m*-nitrobenzoic acid, *m*-azoxybenzoic acid, and m-*azoxybenzyl alcohol*, $ON_2(C_6H_4\cdot CH_2\cdot OH)_2$, which crystallises from benzene in long, yellow needles melting at 86° and forms a *dibenzoyl* derivative melting at 97°; under the action of alcoholic sodium hydroxide, *m*-nitrobenzyl alcohol yields *m*-azobenzoic acid and m-*azobenzyl alcohol*, $N_2(C_6H_4\cdot CH_2\cdot OH)_2$, which crystallises from benzene in beautiful orange needles melting at 106° and forms a *dibenzoyl* derivative crystallising in orange plates and melting at 124°. *p*-Nitrobenzyl alcohol is decomposed by aqueous sodium hydroxide with the formation of *p*-nitrobenzoic acid, *p*-azobenzoic acid, *p*-azobenzyl alcohol, *p*-azobenzaldehyde, and a compound melting at 224°, which is probably identical with *p*-nitrobenzaldoxime-*N*-*p*-formylphenyl-ether, described by Alway (compare Abstr., 1903, i, 706). When acted on by alcoholic sodium hydroxide, the products are *p*-azobenzoic acid and *p*-azobenzyl alcohol, which forms a *dibenzoyl* derivative crystallising from alcohol in red needles melting at 164°. M. A. W.

Action of Magnesium Propyl Iodide on Piperonaldehyde. Efisio Mameli and Ezio Alagna (*Atti R. Accad. Lincei*, 1905, [v], **14**, ii, 170—180. Compare Abstr., 1904, i, 1023; this vol., i, 203).—*Piperonylpropylcarbinol* [α-3 : 4-*methylenedioxyphenylbutane-α-ol*],

$$CH_2<\begin{array}{l}O\cdot C\cdot CH{:}CH \\ O\cdot C\cdot CH{:}C\cdot CHPr^{\alpha}\cdot OH\end{array},$$

prepared by the action of piperonal (0·5 mol.) on magnesium propyl iodide (1 mol.) in ethereal solution with subsequent decomposition by means of ice and dilute sulphuric acid, is a straw-yellow oil boiling at 170—173° under 20 mm. pressure; it is readily oxidised to the corresponding ketone and, when distilled under diminished pressure or treated in the cold with gaseous hydrogen chloride and the product subsequently distilled, it gives α-piperonylbutylene (*vide infra*). The *acetate*, $CH_2O_2{:}C_6H_3\cdot CHPr^{\alpha}\cdot OAc$, is a colourless oil boiling at

197—198° under 25 mm. pressure and dissolves in alcohol, but does not decolorise bromine. When treated with alcoholic potassium hydroxide solution, it yields acetic acid, water, and *a-piperonyl-Δ^{a}-butylene*, $CH_2O_2:C_6H_3\cdot CH:CHEt$, which is a colourless oil with a pleasant odour, is soluble in alcohol, ether, or benzene in all proportions, and boils at 164—166° under 25 mm. or at 258—259° under the ordinary pressure; it is volatile in a current of steam, has the sp. gr. 1·0964 at 15°, and exhibits normal cryoscopic behaviour in benzene solution; it rapidly reduces potassium permanganate and absorbs bromine and hydrogen bromide. With picric acid it combines, giving the *picrate*, $C_{11}H_{12}O_2,C_6H_3O_7N_3$, which crystallises in large, cherry-red prisms melting at 67°.

a-Piperonylbutane, $CH_2O_2:C_6H_3\cdot CH_2Pr^{a}$, prepared by reducing piperonylbutylene by means of sodium in alcoholic solution, is a colourless oil boiling at 246—250°.

aβ-Dibromo-a-piperonylbutane, $CH_2O_2:C_6H_3\cdot CHBr\cdot CHBrEt$, obtained by the action of bromine on piperonylbutylene, is a dark oil which decomposes on distillation.

Piperonyl propyl ketone, $CH_2O_2:C_6H_3\cdot COPr^{a}$, prepared by the oxidation of piperonylpropylcarbinol with chromic acid, separates from alcohol or light petroleum in crystals melting at 47° and is readily soluble in ether or benzene, and to a less extent in acetic acid. Its *oxime*, $C_{11}H_{13}O_3N$, is deposited from alcohol in crystals melting at 75° and is slightly soluble in water and more readily in ether or benzene. The *semicarbazone*, $C_{12}H_{13}O_3N_3$, crystallises from aqueous alcohol in tufts of small needles melting at 193—194°. T. H. P.

Some Derivatives of *cyclo*Hexane. PAUL FREUNDLER and E. DAMOND (*Compt. rend.*, 1905, **141**, 593—594).—Bromo*cyclo*hexane, $C_6H_{11}Br$, prepared by the action of phosphorus tribromide on *cyclo*-hexanol, boils at 61—62° under 20 mm. pressure, and the yield is 68 per cent.; iodo*cyclo*hexane, $C_6H_{11}I$, similarly obtained by the prolonged action of phosphorus di-iodide on *cyclo*hexanol, boils at 84—86° under 23—24 mm. pressure, and the yield is 87 per cent. (compare Baeyer, Abstr., 1894, i, 175). *Ethyl a-cyano*cyclo*hexylacetate*, $C_6H_{11}\cdot CH(CN)\cdot CO_2Et$, obtained by heating the sodium derivative of ethyl cyanoacetate with chloro- or iodo-*cyclo*hexane in xylene solution at 145—150°, is a colourless liquid boiling at 158—161° under 23—24 mm. pressure; *ethyl* cyclo*hexylmalonate*, $C_6H_{11}\cdot CH(CO_2Et)_2$, similarly prepared from the sodium derivative of ethyl malonate, boils at 148—151° under 16—17 mm. pressure. cyclo*Hexylacetic acid* [hexa*hydrophenylacetic acid*], $C_6H_{11}\cdot CH_2\cdot CO_2H$, prepared by heating *cyclo*hexylmalonic acid at 190° or by boiling ethyl *cyclo*cyanoacetate with dilute sulphuric acid, crystallises in white plates melting at 27°, boils at 244—246°, and is readily soluble in the ordinary organic solvents; *ethyl* cyclo*hexylacetate* is a liquid with an agreeable odour boiling at 211—212° under 766 mm. pressure. M. A. W.

Hofmann's Reaction. ERNST MOHR (*J. pr. Chem.*, 1905, [ii], **72**, 297—306. Compare this vol., i, 274; Graebe and Rostovzeff, Abstr., 1902, i, 663; Hantzsch, Abstr., 1903, i, 29).—When one mol. of

benzoylchloroamide is dissolved in one mol. of sodium hydroxide in $2N$ aqueous solution, heat is developed, together with an intense odour of phenylcarbimide; moreover, when a freshly-prepared solution of benzoylchloroamide in aqueous sodium hydroxide is distilled in a current of steam, the distillate contains an oil which solidifies partly in the condenser, forming *s*-diphenylcarbamide; this is found, together with benzoylphenylcarbamide, also in the distillation residue (compare Hofmann, Abstr., 1882, 822; Dam and Aberson, Abstr., 1901, ii, 88). Phenylcarbimide is formed, therefore, as an intermediate product of the action of alkali hydroxides on benzoylchloroamide. Its formation similarly in the action of alkali hydroxides on dibenzhydroxamic acid is proved also by distillation with steam, when diphenylcarbamide is obtained from the distillate. G. Y.

Some Acyl Derivatives of Homoanthranilonitrile [3-Amino-*p*-toluonitrile] and the 4-Keto-7-methyldihydroquinazolines prepared therefrom. Marston T. Bogert and Alfred Hoffman (*J. Amer. Chem. Soc.*, 1905, **27**, 1293—1301. Compare Niementowski, Abstr., 1888, 837; 1889, 1065; 1895, i, 571).—3-Nitro-*p*-toluonitrile crystallises from water in needles of a faint green tint and melts at 99·8° (all the melting points given are corrected). Homoanthranilonitrile (3-amino-*p*-toluonitrile) crystallises from carbon disulphide in large, yellow crystals and melts at 94°.

The following acyl derivatives of homoanthranilonitrile have been prepared by heating the nitrile with acid anhydrides. The *acetyl* derivative, $CN\cdot C_6H_3Me\cdot NHAc$, melting at 136°, the *propionyl* derivative (m. p. 138°), the iso*butyryl* derivative (m. p. 144°), and the iso*valeryl* derivative (m. p. 139°). The following derivatives have been prepared by the action of acyl chlorides on homoanthranilonitrile. The *benzoyl* derivative (m. p. 145°), the m-*nitrobenzoyl* derivative (m. p. 218°), and the p-*nitrobenzoyl* derivative (m. p. 223°). The formyl derivative cannot be obtained by the action of glacial formic acid on homoanthranilonitrile, but 4-keto-7-methyldihydroquinazoline is produced.

When the acyl derivatives of homoanthranilonitrile are heated with a solution of potassium hydroxide and hydrogen peroxide, quinazolines are produced. Acetylhomoanthranilonitrile yields 4-keto-2 : 7-dimethyldihydroquinazoline, whilst the propionyl and *iso*butyryl derivatives furnish 4-keto-2-ethyl- and 2-*iso*propyl-7-methyl-dihydroquinazoline respectively. All these compounds have been described by Niementowski.

4-*Keto*-7-*methyl*-2-iso*butyldihydroquinazoline*,

$$C_6H_3Me<\begin{matrix}N{=}C\cdot C_4H_9\\ \vert \\ CO\cdot NH\end{matrix},$$

crystallises in needles, melts at 219°, and dissolves readily in acetone, acetic acid, or alcohol. 4-*Keto*-2-*phenyl*-7-*methyldihydroquinazoline* crystallises in plates or needles, melts at 243°, and is easily soluble in chloroform, hot benzene, alcohol, or acetic acid. The corresponding 2-m-*nitrophenyl* and 2-p-*nitrophenyl* derivatives form microcrystalline powders, melt sharply above 370°, and are easily soluble in acetone, chloroform, acetic acid, or alcohol. E. G.

Separation of Cinnamic Acid into Stereoisomeric Components. Emil Erlenmeyer, jun. (*Ber.*, 1905, 38, 3499—3503).—The brucine salt of cinnamic acid proved to be homogeneous when prepared in solution in benzene, and melted at 92—93°; by working in alcoholic solution, isomeric crystalline salts were obtained, which differed in melting point and rotatory power; thus samples were obtained having $[\alpha]_D$ 0°, −10·84°, +8·82°, −8·67°, and the melting points 135°, 113°, 135°, 107°. All these salts gave an inactive cinnamic acid, but the author is of opinion that the latter is a mixture of enantiomorphous isomerides the optical activity of which is too small to be measured. T. M. L.

Second Stereoisomeric Component of *allo*Cinnamic Acid. Emil Erlenmeyer, jun. (*Ber.*, 1905, 38, 3496—3499).—The crystalline brucine salt derived from *allo*cinnamic acid (this vol., i, 646) yields an acid which differs in a marked way from the *iso*cinnamic acid isolated by Liebermann from the coca plant. The acid contained in the more soluble brucine salt has now been investigated, and proved by crystallographic measurements to be identical with Liebermann's acid. Although neither acid shows a measurable optical activity, they are regarded by the author as optical isomerides; this conclusion is based in part on the observation that the brucine salts differ considerably in rotatory power, namely, $[\alpha]_D$ −24·89° and −13·98°.
T. M. L.

Action of Hippuryl Chloride on Polyhydric Phenols. Emil Fischer (*Ber.*, 1905, 38, 2926—2934. Compare this vol., i, 263).—o-*Hydroxyphenyl hippurate*, $NHBz\cdot CH_2\cdot CO\cdot O\cdot C_6H_4\cdot OH$, is formed when hippuryl chloride is heated with catechol on the water-bath; it crystallises from water in delicate, colourless leaflets, melts at 134—136° (corr.), is readily soluble in alcohol or dilute alkali hydroxides, and is easily hydrolysed by warm dilute acids or alkali hydroxides or by cold concentrated sulphuric acid. When treated with hydrogen chloride in a tube cooled by liquid air, then sealed and kept at 20—30° for 16 days, it forms the *anhydro*-derivative, $C_{15}H_{11}O_3N$, which crystallises from ethyl acetate in colourless, slender needles, sinters at 226° (corr.), and melts at 232—233° (corr.); it gives with alcoholic ferric choride a dark coloration, and on addition of water a deep brownish-red precipitate, decolorises alkaline potassium permanganate at the ordinary temperature, and remains almost unchanged when heated with hydrogen chloride in glacial acetic acid solution in a sealed tube at 100°.

When heated with hippuryl chloride on the water-bath, resorcinol forms one dihippuryl and two monohippuryl derivatives. The *α-hippuryl* derivative, $C_{15}H_{13}O_4N$, which is extracted from the reaction-product by means of cold ethyl acetate, crystallises on concentration of the solution, melts at 144° (corr.), is decomposed by aqueous alkali hydroxides, and is hydrolysed with formation of hippuric acid when boiled with dilute hydrochloric acid. The *β-hippuryl* derivative crystallises from alcohol in colourless, slender needles, commences to decompose at 255° (corr.), and when quickly heated melts at about

274° (corr.); it dissolves in dilute sodium hydroxide and is precipitated unchanged on acidification, gives a brownish-red coloration with alcoholic ferric chloride, and is much more stable than the α-isomeride towards boiling hydrochloric acid. The *dihippuryl* derivative, $C_{24}H_{20}O_6N_2$, remains after successive treatment of the reaction product with cold ethyl acetate and dilute sodium hydroxide; it crystallises from hot ethyl acetate in glistening leaflets, melts at 179—180° (corr.), is readily soluble in alcohol, but only sparingly so in hot water or ether, is decomposed by boiling dilute alkali hydroxides, and dissolves in cold concentrated sulphuric acid, from which it is precipitated unchanged on dilution. Hippuryl chloride reacts with quinol at 125—130° to form hippuryl and dihippuryl derivatives of quinol. The *hippuryl* derivative, $C_{15}H_{13}O_4N$, crystallises from water in glistening needles, melts at 155—157° (corr.), is readily soluble in cold alcohol, ethyl acetate, hot glacial acetic acid, or dilute alkali hydroxides, and is easily hydrolysed by boiling hydrochloric acid with formation of hippuric acid. The *dihippuryl* derivative, $C_{24}H_{20}O_6N_2$, crystallises from boiling alcohol in glistening, white leaflets, commences to sinter at 214° (corr.), and melts and decomposes at 220—222° (corr.); it is only sparingly soluble in hot water, boiling alcohol, ether, acetone, or hot toluene, and is hydrolysed with formation of hippuric acid by boiling aqueous alkali hydroxides. G. Y.

Action of Potassium Hypochlorite, Hypobromite, and Hypoiodite on Dipotassium Salicylate. LASSAR-COHN and FRITZ SCHULTZE (*Ber.*, 1905, **38**, 3294—3302).—When ice-cold aqueous solutions of potassium hypobromite and dipotassium salicylate are mixed in molecular proportions and the mixture acidified, the products are 6-*bromo*- and 5 : 6-*dibromosalicylic acid*. These may be separated by means of their ammonium salts, as *ammonium* 5 : 6-*dibromosalicylate* is very sparingly soluble in water, 0·44 gram dissolving in 100 c.c. of water at 16°. The monobromo-acid melts at 161° and begins to sublime at 100°; the dibromo-acid melts at 227·5°, and when heated for 24 hours at 280° with concentrated hydrochloric acid yields 3 : 4-dibromophenol. The *methyl* ester melts at 156°. Neither acid can be esterified by the hydrogen chloride catalytic method.

When an excess (2—4 mols.) of the hypobromite is used, a certain amount of *s*-tribromophenol is formed, but no monobromo-acid.

Potassium hypochlorite yields a mixture of 6-*chloro*- and 5 : 6-*dichloro-salicylic acids*, which can also be separated by means of their ammonium salts. The dichloro-acid melts at 223°, is sparingly soluble in water, cannot be esterified by Fischer and Speier's method, and is not decomposed when heated with hydrochloric acid at 300°. When fused with potassium hydroxide and nitrated, it yields a *dichloronitrophenol* melting at 125°. The *barium* salt is anhydrous and crystallises from water, and the *methyl* ester melts at 150°. The monochloro-acid melts at 176° and when heated with hydrochloric acid yields *m*-chlorophenol. When 4 mols. of the hypochlorite are used, considerable quantities of *s*-trichlorophenol are produced.

The product obtained by mixing molecular proportions of potassium hypoiodite and dipotassium salicylate, then adding potassium hydrogen

sulphite and fractionally precipitating with acid, is 4-*iodosalicylic acid.* This melts at 199·5° and when heated with hydrochloric acid at 300° yields *m*-iodophenol. The *aniline* salt, $OH\cdot C_6H_3I\cdot CO_2\cdot NH_3Ph$, melts at 138° and the *methyl* ester at 80°. J. J. S.

Benzoyl Derivatives of Salicylamide. KARL AUWERS (*Ber.*, 1905, **38**, 3256—3259).—A discussion of Titherley and Hicks' paper (*Trans.*, 1905, **87**, 1207). The author considers that the labile benzoyl derivative of salicylamide has the constitution $OBz\cdot C_6H_4\cdot CO\cdot NH_2$, whilst the stable isomeride, melting at 208°, is the *N*-benzoyl derivative, $OH\cdot C_6H_4\cdot CO\cdot NHBz$. G. Y.

Carbonates of Salicylonitrile and of Salicylaldehyde. ALFRED EINHORN and GUSTAV HAAS (*Ber.*, 1905, **38**, 3627—3632. Compare Abstr., 1903, i, 30).—*Salicylonitrile carbonate,* $CO(O\cdot C_6H_4\cdot CN)_2$, is obtained by shaking a toluene solution of carbonyl chloride with a solution of salicylonitrile in sodium hydroxide and adding light petroleum to the toluene solution. It crystallises from alcohol in colourless, felted needles, melts at 116°, and dissolves readily in benzene, chloroform, or ether. When warmed with water or left in contact with alkalis, it is slowly decomposed, yielding salicylonitrile. It is readily decomposed when warmed with absolute alcohol, yielding salicylonitrile and *ethyl salicylonitrile carbonate,*

$$CO(O\cdot C_6H_4\cdot CN)_2 + EtOH = CN\cdot C_6H_4\cdot O\cdot CO_2Et + OH\cdot C_6H_4\cdot CN.$$

The latter crystallises in needles, melts at 47°, is insoluble in water, but dissolves readily in alcohol or ether.

Hydrogen peroxide reacts with a cold alcoholic solution of the carbonate, yielding salicylonitrile. Concentrated sulphuric acid converts the carbonate of the nitrile into salicylamide carbonate.

When salicylaldehyde is warmed with a pyridine solution of carbonyl chloride, disalicylaldehyde is formed; with a solution of sodium hydroxide instead of pyridine, *salicylaldehyde carbonate,* $CO(O\cdot C_6H_4\cdot CHO)_2$, is obtained. It crystallises from light petroleum in colourless, felted needles, or from carbon tetrachloride in large rhombohedra melting at 88—89°. It dissolves readily in acetone, benzene, chloroform, or ethyl acetate, but only sparingly in alcohol. It cannot be oxidised to the corresponding carbonate of salicylic acid.

The *dioxime,* $CO(O\cdot C_6H_4\cdot CH{:}N\cdot OH)_2$, crystallises from methyl alcohol in colourless needles melting at 121—122°. It dissolves readily in most organic solvents and is decomposed by sodium hydroxide. The *bisphenylhydrazone,* $C_{27}H_{22}O_3N_2$, crystallises in yellow plates and melts at 179—180°. The dihydrazone and disemicarbazone could not be prepared.

The conversion of Titherley and Hicks' *O*-benzoylsalicylamide melting at 144° into the isomeride melting at 208° (Trans., 1905, **87**, 1207) is regarded as the conversion of an *O*- into an *N*-benzoyl derivative. (Compare Auwers, preceding abstract.) J. J. S.

Constitution of the Aromatic Purpuric Acids. VII. Ethyl 3:5-dinitrosalicylate and Potassium Cyanide. WALTHER BORSCHE and G. GAHRTZ (*Ber.*, 1905, **38**, 3538—3542. Compare Abstr., 1904, i, 166, 574; this vol., i, 51).—Ethyl 5-nitro-4-cyano-3-

hydroxylamino-2-hydroxybenzoate, formed by reducing dinitrosalicylic ester with potassium cyanide, can be purified by crystallising from ethyl alcohol; it then forms reddish-brown scales and melts at 186°. Saponification not only separates alcohol, but results in the addition of a molecule of water to the cyano-group,

$$NO_2\cdot C_6H(CN)(NH\cdot OH)(OH)\cdot CO_2Et \longrightarrow NO_2\cdot C_6H(CO\cdot NH_2)(NH\cdot OH)(OK)\cdot CO_2K;$$

the *potassium* salt separates with $1H_2O$; the free nitrocarbamidohydroxylaminohydroxybenzoic acid separates from alcohol in blood-red needles and melts at 187—188°.

The original ester is oxidised by nitric acid to *ethyl* 3 : 5-*dinitro*-4-*cyano-salicylate*, $OH\cdot C_6H(NO_2)_2(CN)\cdot CO_2Et$, which crystallises from alcohol or acetic acid in stout, dark red needles and melts at 187°. The *ammonium* salt was prepared and analysed. The *aniline* salt of the ester crystallises in slender, red needles and melts at 162°.

Sulphuric acid causes the original ester to undergo isomeric change (compare β-phenylhydroxylamine ⟶ *p*-aminophenol). The product, *ethyl* 5-*nitro*-3-*amino*-4-*cyano*-2 : 6-*dihydroxybenzoate*,

$$NO_2\cdot C_6(OH)_2(CN)(NH_2)\cdot CO_2Et,$$

crystallises from alcohol in brownish-red needles and melts at 199—200°; the *ammonium* salt, $C_{10}H_8O_6N_3\cdot NH_4$, forms slender, red needles. The isomeric change here recorded affords the first proof of the presence of a hydroxylamino-group in the aromatic purpuric acids.

T. M. L.

o-Benzoylbenzoic Acid. Hugo Lang (*Monatsh.*, 1905, **26**, 971—976. Compare Basler Chemische Fabrik, Abstr., 1904, i, 512; Kliegl, this vol., i, 187).—4-Nitro-2-benzoylbenzoic acid is formed when anhydrous *o*-benzoylbenzoic acid is added to nitric acid of sp. gr. 1·52, cooled by ice, and after four to five hours the reaction product poured into ice-water; after recrystallisation from benzene, it melts at 160—161° (m. p. 161·5—162°; Kliegl, *loc. cit.*), but on recrystallisation from alcohol forms yellow prisms and melts at 183—184°. The methyl ester, formed by boiling the acid with methyl alcohol and a few c.c. of concentrated sulphuric acid, melts at 105°. The isomeric *methyl* ester, obtained by Meyer's thionyl chloride method (Abstr., 1904, i, 747), crystallises in large, monoclinic prisms and melts at 131°. 4-*Nitro-2-benzoylbenzoyl chloride*, formed by the action of thionyl chloride on the acid, decomposes at 127—129°, or on exposure to the air.

The action of nitric acid of sp. gr. 1·52 on methyl *o*-benzoylbenzoate leads to the formation of a *dinitro*-derivative, $C_{15}H_{10}O_7N_2$, which crystallises in glistening, white leaflets, melts and decomposes at 136°, and is readily soluble in alcohol, chloroform, or hot benzene.

G. Y.

Esterification of Unsymmetrical Di- and Poly-basic Acids. XIII. Ester-acids of 4-Substituted Phthalic Acids. Rudolf Wegscheider and Erich Bondi (*Monatsh.*, 1905, **26**, 1039—1068. Compare Wegscheider and Lipschitz, Abstr., 1901, i, 32; Wegscheider, Abstr., 1902, i, 618; Wegscheider and Piesen, *ibid.*, i, 619; Weg-

scheider and Kušy von Dúbrav, Abstr., 1904, i, 244).—Contrary to the statements of Miller (Abstr., 1878, 982) and of Bogert and Boroschek (Abstr., 1902, i, 98), the action of ethyl alcohol and hydrogen chloride on 4-nitrophthalic acid and of ethyl alcohol on the anhydride of 4-nitrophthalic acid leads to the formation of the 1-monoethyl ester melting at 127—128°. Only by the latter method of esterification could be isolated a small quantity of the 2-monoethyl ester melting at 137°. Bogert and Boroschek's substance melting at 141—150° was a mixture.

1-Ethyl hydrogen 4-nitrophthalate $[CO_2Et : CO_2H : NO_2 = 1 : 2 : 4]$ crystallises in monoclinic plates $[a : b : c = 1{\cdot}7447 : 1 : 1{\cdot}4277;\ \beta = 118°31']$.

The *ψ-ethyl* ester of 5-nitrophthalaldehydic acid,

$$NO_2{\cdot}C_6H_3{<}\genfrac{}{}{0pt}{}{CO}{CH(OEt)}{>}O,$$

is formed by boiling the acid with alcohol in a reflux apparatus; it crystallises from a mixture of benzene and light petroleum in sheaves of needles and melts at 95°. The true *ethyl* ester,

$$NO_2{\cdot}C_6H_3(COH){\cdot}CO_2Et,$$

is formed, along with a yellow, amorphous substance which softens at 145° and melts at 160°, and decomposes with evolution of a gas at 165—170°, by the action of ethyl iodide on the silver salt. It crystallises from a mixture of benzene and light petroleum in slender, colourless needles, melts at 71—72°, and is oxidised by potassium permanganate to 2-ethyl hydrogen 4-nitrophthalate $[CO_2H : CO_2Et : NO_2 = 1 : 2 : 4]$, which melts at 137°.

When reduced with stannous chloride and hydrochloric acid or with zinc dust and methyl-alcoholic hydrochloric acid, 1-methyl hydrogen 4-nitrophthalate yields 1-*methyl hydrogen* 4-*aminophthalate*, $C_9H_9O_4N$, which is obtained on evaporation of its blue, fluorescent ethereal solution as a yellow, crystalline substance; different fractions melted at from 110° to 145°. When diazotised in dilute sulphuric ester and warmed finally at 100°, the amino-ester yields 1-*methyl hydrogen* 4-*hydroxyphthalic acid*, $C_9H_8O_5$, which is obtained as a slightly yellow, crystalline substance decomposing at 159—160°; this is isomeric with Wegscheider and Piesen's α-ester melting at 166° (*loc. cit.*). G. Y.

Nitro-derivatives of Fluorescein. MARSTON T. BOGERT and RALPH GARRIGUE WRIGHT (*J. Amer. Chem. Soc.*, 1905, **27**, 1310—1316). —This work was undertaken with the object of ascertaining the influence of nitro- and amino-groups on the fluorescence of fluorescein.

3- and 4-Nitrofluoresceins, obtained by the interaction of resorcinol with 3-nitrophthalic acid and 4-nitrophthalic acid respectively, dissolve in alkalis to form yellowish-red solutions with a weak but distinct green fluorescence.

Dinitrofluorescein (Hewitt and Perkin, Trans., 1900, **77**, 1324) dissolves in alkali with formation of a deep blue solution which shows no fluorescence.

An attempt was made to prepare tetranitrofluorescein (Baeyer, this Journal, 1877, i, 200, and Hewitt and Perkin, *loc. cit.*) by the action of fuming nitric acid on a solution of fluorescein in sulphuric acid. The

product crystallised from acetone as a white powder with a distinct yellowish-green fluorescence, and on analysis gave results agreeing with those required for a pentanitro- rather than a tetranitro-compound. The acetyl derivative of this compound furnished analytical data corresponding with those required for a pentanitrotetra-acetylfluorescein.

When 4-nitrofluorescein is reduced with stannous chloride and hydrochloric acid, a *substance*, probably the aminofluorescein, is formed which melts at 281° and dissolves in alkalis with a green fluorescence. On reducing 3-nitrofluorescein, a product was obtained which gave a fluorescent solution in alkali, but the amino-derivative itself could not be isolated.

By the reduction of dinitrofluorescein with stannous chloride and hydrochloric acid, a *substance* is obtained which crystallises from alcohol in blue plates with brilliant, bronze-green lustre, melts at 198—199°, is slightly soluble in ether or glacial acetic acid, forming solutions with a strong, green fluorescence, and in dilute alkalis with production of red solutions with violet fluorescence. When an alcoholic solution of dinitrofluorescein is reduced with stannous chloride and dry hydrogen chloride, a *substance* is produced which forms bright yellow crystals and melts at 249°.

By the action of various reducing agents on pentanitrofluorescein, deep red solutions were obtained which, on dilution, showed a blue fluorescence, but no pure reduction product could be isolated.

E. G.

Products obtained by the Autoxidation of Eosin. ARTHUR HEFFTER (*Ber.*, 1905, **38**, 3633—3634. Compare Gros, Abstr., 1901, ii, 433).—When a 0·5 per cent. eosin solution containing 1 per cent. of sodium hydroxide is exposed to sunlight, and air is passed through the solution until the fluorescence has completely disappeared and the red colour has been bleached to a pale yellow, no precipitate is obtained and the solution is found to contain sodium bromide, carbonate, oxalate, and phthalate. From 30 grams of eosin, 1·1 grams of phthalic acid were obtained.

J. J. S.

Formation of $\alpha\beta$-Dihydrocinnamylidenemalonic Acid and $\alpha\beta$-Dihydrocinnamylideneacetic Acid. EMIL ERLENMEYER, jun. and ADOLF KREUTZ (*Ber.*, 1905, **38**, 3503—3505).—*$\alpha\beta$-Dihydrocinnamylidenemalonic acid*, prepared by condensing styryl chloride with ethyl malonate and saponifying the ester, separates from benzene in slender needles and decomposes at 132°, thus differing essentially from the $\alpha\delta$- and $\gamma\delta$-acids. On heating to drive off carbon dioxide, an acid is obtained identical with the $\alpha\beta$-dihydrocinnamylideneacetic acid described by Fichter and Baur (Abstr., 1898, i, 662) and by Riiber (this vol., i, 777).

T. M. L.

Two Dehydropinacones of Artemisin (Artemisone and *iso*-Artemisone). PASQUALE BERTOLO and G. RANFALDI (*Gazzetta*, 1905, **35**, ii, 235—244. Compare Bertolo, Abstr., 1902, i, 814).—The reduction of artemisin by means of zinc dust and acetic acid yields a bishypo-artemisin, which the authors term *artemisone*, of the com-

position $C_{30}H_{34}O_6$. It separates from alcohol in minute, white crystals, to some extent grouped in small, mammillary masses, and melts at 273—274°. It dissolves slightly in ether, light petroleum, or chloroform, and more readily in acetic acid, in which it has $[\alpha]_D$ +159°. Artemisone preserves the lactonic character of artemisin and dissolves in alkaline hydroxide solutions forming salts of a dibasic acid, *artemisonic acid*, which, unlike the corresponding acid obtained from santonone, is only slightly stable in the free state, as it gradually loses water and becomes converted into iso*artemisone* (*vide infra*). The *barium*, $C_{30}H_{36}O_8Ba$, and *silver* salts, $C_{30}H_{36}O_8Ag_2$, of artemisonic acid were prepared and analysed. With salts of the heavy metals, artemisonic acid gives variously coloured precipitates.

*iso*Artemisone is a lactone isomeric with artemisone and is best prepared by decomposing barium artemisonate by means of hydrochloric acid. It separates from a mixture of light petroleum and ether in minute, white crystals melting at 182—183°. It has the normal molecular weight in freezing acetic acid and has $[\alpha]_D$ −157° in alcohol and −153° in glacial acetic acid. It is soluble in solutions of the alkali hydroxides or carbonates and is precipitated unchanged on addition of an acid. Like artemisone, it does not react with hydroxylamine, phenylhydrazine, or acetic anhydride.

On the supposition that artemisone and *iso*artemisone were enantiomorphous compounds, attempts were made to prepare the corresponding racemic compound, but these were unsuccessful.

T. H. P.

Dibenzoylethane-2 : 2′-dicarboxylic Acid and its Anhydride. ARNOLD REISSERT and W. ENGEL (*Ber.*, 1905, **38**, 3281—3294).—*Dibromoethinediphthalide*, $CO<\genfrac{}{}{0pt}{}{C_6H_3Br}{O}>C:C_2H_2:C<\genfrac{}{}{0pt}{}{C_6H_3Br}{O}>CO$, is formed by heating dibenzoylethane-2 : 2′-dicarboxylic acid with bromine in a sealed tube at 100° for 24 hours; it does not melt at 350°, and does not lose bromine when boiled with concentrated aqueous potassium hydroxide, aniline, or alcoholic ammonia. When boiled with 20 per cent. aqueous potassium hydroxide, it yields *dibromobenzoylethane-2 : 2′-dicarboxylic acid*,

$$CO_2H\cdot C_6H_3Br\cdot CO\cdot CH_2\cdot CH_2\cdot CO\cdot C_6H_3Br\cdot CO_2H,$$

which melts above 350°.

When dissolved in nitric acid of sp. gr. 1·5, dibenzoylethane-2 : 2′-dicarboxylic acid yields a *substance* which crystallises in large, monoclinic plates, decomposes and evolves nitric oxide at about 90°, after resolidification melts at 196—200°, and when treated with sodium carbonate forms Roser's β-anhydride melting at 202° (Abstr., 1886, 243). This is formed also, sometimes together with a mixture melting at 220—230°, when the acid is boiled with acetic anhydride, or together with ethinediphthalide, when the acid is heated with hydrogen chloride in glacial acetic acid solution or with an excess of concentrated hydrochloric acid at 100° for four hours. When heated with concentrated hydrochloric acid at 100° for nine hours, the acid yields traces of a yellow *substance* melting at 225—230°, together with ethinediphthalide. The β-anhydride remains unchanged when

boiled for a short time with acetic anhydride, or glacial acetic and concentrated hydrochloric acids, or with glacial acetic and concentrated sulphuric acids. It melts without change, but when heated to the boiling point or dissolved in concentrated sulphuric acid it yields ethinephthalide, into which it is partly converted when boiled with an excess of concentrated hydrochloric acid for nine hours. Ethinephthalide is formed also when dibenzoylethane-2 : 2′-dicarboxylic acid is dissolved in a mixture of acetic anhydride and concentrated sulphuric acid or is warmed with the latter. The *dianil*,

$$C_6H_4<\begin{matrix}C(NPh)\cdot C_2H_4\cdot C(NPh)\\ CO\text{———}O\text{———}CO\end{matrix}>C_6H_4,$$

is formed when the anhydride is heated with aniline on the water-bath; it crystallises from alcohol, decomposes at 190—191°, is easily soluble in glacial acetic acid, and only sparingly so in benzene, dissolves without formation of aniline in boiling sodium carbonate solution, and is hydrolysed by boiling sodium ethoxide solution.

Ethinediphthalidedianil, $CO<\begin{matrix}C_6H_4\\ NPh\end{matrix}>C:CH\cdot CH:C<\begin{matrix}C_6H_4\\ NPh\end{matrix}>CO$, is obtained when the anhydride is heated with aniline for three hours at 150—160°; it separates from glacial acetic acid in yellow crystals, melts at 310—311°, is stable towards alkali hydroxides and acids, and may be identical with Roser's diphthalylsuccindehydranilide (Abstr., 1886, 244). The *di*-o-*tolil*, $C_{32}H_{24}O_2N_2$, crystallises in stout, yellow needles and melts at 286—287°. The *di*-p-*tolil* melts at 294—295°. The *bisphenylhydrazone*,

$$C_6H_4<\begin{matrix}C(N_2HPh)\cdot C_2H_4\cdot C(N_2HPh)\\ CO\text{————}O\text{————}CO\end{matrix}>C_6H_4,$$

formed when the anhydride is warmed with an excess of phenylhydrazine, is a colourless, crystalline substance, which melts at 242°, and dissolves in alcoholic potassium hydroxide, but after some time separates from the solution unchanged.

When warmed with nitric acid of sp. gr. 1·4, bisphenylphthalazonylethane, melting at 236—237°, yields a *dinitronitroso*-derivative, $C_{30}H_{19}O_7N_7$, which melts at 316—318°, and on reduction with stannous chloride forms a *base* which melts at 251—253°.

Bis-p-*nitrophenylphthalazonylethane*,

$$\begin{matrix}CO\text{———}C_6H_4\\ |\qquad\qquad\\ N(C_6H_4\cdot NO_2)\cdot N\end{matrix}>C\cdot CH_2\cdot CH_2\cdot C<\begin{matrix}C_6H_4\cdot CO\\ \qquad\quad |\\ N\text{——}N\cdot C_6H_4\cdot NO_2\end{matrix},$$

formed by boiling dibenzoylethanedi-*o*-carboxylic acid with *p*-nitrophenylhydrazine in alcoholic solution, melts above 350°.

1-*Phenylmethylaminopyrrole*-2 : 5-*dibenzoic acid*,

$$NMePh\cdot N<\begin{matrix}C(C_6H_4\cdot CO_2H):CH\\ |\\ C(C_6H_4\cdot CO_2H):CH\end{matrix},$$

is obtained by boiling dibenzoylethane-2 : 2′-dicarboxylic acid with phenylmethylhydrazine in alcoholic solution in a reflux apparatus; it crystallises in slightly brown, stout needles and melts at 205—206°. If the acid is boiled with phenylmethylhydrazine in a limited quantity of alcohol, it forms the *anhydride*, $NMePh\cdot N<\begin{matrix}C{-}C_6H_4\cdot CO\\ >C_2H_2\qquad\\ C{-}C_6H_4\cdot CO\end{matrix}>O$, which

crystallises in stout, yellow needles, melts at 205—206°, and is hydrolysed by aqueous alkali hydroxides. The *sodium* salt, $C_{25}H_{18}O_4N_2Na_2$, crystallises in thin, white leaflets; the *silver* salt, $C_{25}H_{18}O_4N_2Ag_2$, was analysed; the *diethyl* ester, crystallises in concentric aggregates of needles and melts at 90—91°. When treated with cooled concentrated sulphuric acid, the acid is decomposed with formation of methylaniline and *pyrrole*-2:5-*dibenzoic acid*, which is obtained as an amorphous substance melting and decomposing at 195° (compare Gabriel, *Ber.*, 1886, **19**, 841).

1-*Phenylbenzylaminopyrrole*-2:5-*dibenzoic acid*, $C_{31}H_{24}O_4N_2$, formed by boiling dibenzoylethane-2:2′-dicarboxylic acid with phenylbenzylhydrazine in alcoholic solution, crystallises from dilute alcohol and melts at 218—219°. The *silver* salt, $C_{31}H_{22}O_4N_2Ag_2$, was analysed; the *diethyl* ester, $C_{35}H_{32}O_4N_2$, crystallises in slender, white needles and melts at 101—102°. When treated with concentrated sulphuric acid, the acid is decomposed with formation of pyrrole-2:5-dibenzoic acid, melting at 195°. G. Y.

Ellagic Acid. GUIDO GOLDSCHMIEDT (*Monatsh.*, 1905, **26**, 1139—1148. Compare Goldschmiedt and Jahoda, Abstr., 1892, 990; Perkin and Nierenstein, Trans., 1905, **87**, 1412).—When boiled with phenylhydrazine in alcoholic solution, or when carefully heated with phenylhydrazine in absence of a solvent, ellagic acid forms the *product* $C_{14}H_6O_8,N_2H_3Ph$, which crystallises in microscopic, yellow needles, is decomposed partially when boiled with alcohol, and yields ellagic acid on addition of acetic acid to its suspension in water. Ellagic acid forms similar compounds with aniline and quinoline; the air-dried *product* with quinoline has the formula $2C_{14}H_6O_8,C_9H_7N$.

The etherification of ellagic acid by means of alkyl iodides and alcoholic alkali hydroxides takes place extremely slowly, and part of the acid undergoes decomposition; slightly better results are obtained by heating ellagic acid with alkyl iodides and aqueous potassium hydroxide at 150—160° under pressure. *Ellagic acid methyl ether*, $C_{14}H_5O_7\cdot OMe$, formed in this manner, is obtained as a yellow, crystalline powder which decomposes without melting when heated gives no coloration with ferric chloride, and forms a *diacetate*, $C_{14}H_3O_7Ac_2\cdot OMe$; this separates as a white, crystalline powder and melts when heated. *Ellagic acid dimethyl ether*, $C_{14}H_4O_6(OMe)_2$, formed in small quantity on prolonged heating of ellagic acid with methyl iodide and aqueous potassium hydroxide at 150—160°, is obtained as an insoluble, microcrystalline powder, which dissolves in concentrated sulphuric acid, from which it gradually separates in white crystals, and gives no coloration with ferric chloride.

The repeated action of diazomethane on ellagic acid in ethereal solution leads to the formation of *ellagic acid tetramethyl ether*, $C_{14}H_2O_4(OMe)_4$; this slowly separates from its solution in aqueous alkali hydroxides, on neutralisation with carbon dioxide or mineral acids and warming, in hair-like, almost colourless, microscopic needles which remain unchanged at 310°, is insoluble or almost so in aromatic hydrocarbons, alcohol, ether, chloroform, or carbon disulphide, dissolves in concentrated sulphuric acid to form a yellowish-green solution, from

which it separates in white crystals on dilution with water, gives no coloration with ferric chloride, and when warmed with phenylhydrazine dissolves, but separates again unchanged on cooling.

These properties of ellagic acid agree with Graebe's formula for this substance (Abstr., 1903, i, 262). G. Y.

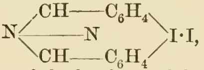
Di-*p*-benzaldehydeiodonium Hydroxide and its Derivatives. Conrad Willgerodt and Hans Bogel (*Ber.*, 1905, **38**, 3446—3451). —*Di*-p-*benzaldehydeiodonium hydroxide*, $COH\cdot C_6H_4\cdot I(OH)\cdot C_6H_4\cdot CHO$, prepared by the action of silver oxide on a mixture of iodoso- and iodoxybenzaldehyde, is obtained as an uncrystallisable solid. The *chloride* crystallises in colourless needles and melts at 180°; the *bromide* forms very minute, colourless needles and melts at 151°; the *iodide* crystallises from water in golden-yellow needles and prisms and melts at 138° to a bright yellow liquid; the *periodide* forms black needles aggregated in rosettes and bunches, which, on heating, soften to a dark liquid at 102°. The *dichromate* is obtained as a reddish-yellow, crystalline powder which decomposes very rapidly. The *platinichloride* separates from dilute aqueous solutions in golden-yellow prisms and decomposes to a black liquid at 170°; the *mercurichloride* forms colourless needles decomposing at 160—168°.

Di-p-*benzaldehydeiodonium iodide diphenylhydrazone*,

$$NHPh\cdot N\colon CH\cdot C_6H_4\cdot I_2\cdot C_6H_4\cdot CH\colon N\cdot NHPh,$$

is obtained as a reddish-yellow, amorphous powder which decomposes at 115—125° to a red liquid. The *di-semicarbazone* crystallises from alcohol in almost colourless needles melting at 218°.

Di-p-*benzaldehydeiodonium iodide azine*,



prepared by the action of hydrazine sulphate on dibenzaldehydeiodinium iodide, separates as a yellow precipitate, insoluble in ordinary solvents, which begins to decompose about 200°.

The *benzidine* derivative, $N{<}{\substack{C_6H_4—C_6H_4—N \\ CH\cdot C_6H_4\cdot I_2\cdot C_6H_4}}{>}CH$, crystallises from nitrobenzene in yellow leaflets which decompose above 300° and become dark red when exposed for a long time to the atmosphere.

E. F. A.

***p*-Iodobenzaldehyde, *p*-Iodobenzophenone, and Derivatives of the Latter containing Polyvalent Iodine.** Conrad Willgerodt and Hans Bogel (*Ber.*, 1905, **38**, 3451—3458).—p-*Iodobenzaldehyde*, prepared by the interaction of diazotised *p*-anhydroaminobenzaldehyde with potassium iodide, forms snow-white crystals melting at 78°; p-*iodobenzylideneaniline*, $C_6H_4I\cdot CH\colon NPh$, crystallises from alcohol in large, light yellow leaflets melting at 89—91°. p-*Iodobenzophenone*, $C_6H_4I\cdot COPh$ prepared by the interaction of iodobenzaldehyde with magnesium phenyl bromide, treatment of the resulting compound with water to form *p*-iodobenzhydrol, and subsequent oxidation of this with potassium dichromate, crystallises in well-formed, colourless needles melting at 100—101°.

p-*Benzophenone iododichloride*, $C_6H_5\cdot CO\cdot C_6H_4\cdot ICl_2$, separates in faintly greenish-yellow, monoclinic plates and loses its chlorine above 90°. p-*Iodosobenzophenone*, $C_6H_5\cdot CO\cdot C_6H_4\cdot IO$, is obtained as an amorphous, yellow or orange powder which sinters at 150° and is completely melted at 180°; the *acetate* crystallises in long needles aggregated in bunches and melts at 168°.

p-*Iodoxybenzophenone*, $C_6H_5\cdot CO\cdot C_6H_4\cdot IO_2$, is a colourless, odourless, sandy powder which explodes faintly when heated on platinum foil.

p-*Benzophenone phenyliodonium hydroxide*,

$$C_6H_5\cdot CO\cdot C_6H_4\cdot IPh\cdot OH,$$

is obtained in the form of an alkaline, yellow solution by the interaction of benzophenone iododichloride and mercurydiphenyl and treatment of the resulting iodonium iodide with silver oxide and water. The *chloride* crystallises in colourless, glistening needles melting at about 200°; the *bromide* forms small, colourless needles melting at 157°; the *iodide* is sparingly soluble in water, separates in light yellow needles, and melts at 138°; the *dichromate* crystallises in long, orange-yellow needles and decomposes above 120°. The *platinichloride* crystallises in small, yellow prisms and decomposes at 180°; the *mercurichloride* crystallises in colourless needles and melts at 147—150°.

E. F. A.

Dibromides of Aromatic Propenyl Compounds. III. Behaviour of Anethole Dibromide and *iso*Safrole Dibromide on Oxidation. Paul Hoering (*Ber.*, 1905, 38, 3458—3463. Compare Abstr., 1904, i, 577; this vol., i, 592).—On oxidation of anethole dibromide with concentrated nitric acid in the cold, a colourless substance crystallising in needles and melting at 98—99° is obtained, and is probably *β-?-dibromo-α-ketodihydroanethole*,

$$OMe\cdot C_6H_3Br\cdot CO\cdot CHBrMe,$$

together with an oil which is a mixture of the above substance and *β-?-dibromonitro-α-ketodihydroanethole*,

$$OMe\cdot C_6H_2Br(NO_2)\cdot CO\cdot CHMeBr,$$

melting at 92°. With chromic acid, in the main, the above bromoanethole ketobromide is obtained, mixed with anethole ketobromide; permanganate gives a similar result.

By the action of nitric acid on β-?-dibromo-α-methoxydihydroanethole, the above bromoanetholeketobromide is formed; from β-bromo-α-methoxydihydroanethole, the β-bromonitro-α-ketodihydroanethole, melting at 94—95°, mixed with some dinitro-compound, was obtained.

*β-Bromonitro-α-acetoxydihydro*iso*safrole*,

$$CH_2O_2\colon C_6H_2(NO_2)\cdot CH(OAc)\cdot CHMeBr,$$

prepared by the action of nitric acid on *iso*safrole dibromide in glacial acetic acid, forms yellow, prismatic needles melting at 113°; nitro*iso*safroleoxide, $CH_2O_2\colon C_6H_2(NO_2)<\overset{CH}{\underset{O}{}}>CHMe$, is formed on hydrolysis, and reacts with alcoholic potassium hydroxide to form a *compound*, melting at 134—135°, soluble in alkali hydroxides.

E. F. A.

Dibromides of Aromatic Propenyl Compounds. IV. Substitution in and Elimination of Bromine Atoms from Dibromides. PAUL HOERING (*Ber.*, 1905, 38, 3464—3476. Compare preceding abstract).—*β-Bromo-α-methoxydihydro*iso*safrole*,

$CH_2O_2{:}C_6H_3{\cdot}CH(OMe){\cdot}CHBrMe$,

is a colourless, strongly refractive oil boiling at 166—169° under 11 mm. and at 158—164° under 8 mm. pressure; the *α-ethoxy*-derivative is a colourless oil, which boils at 175—178° under 18 mm. and at 165—170° under 10 mm. pressure,

*β-?-Tribromo-α-methoxydihydro*iso*safrole*,

$CH_2O_2{:}C_6HBr_2{\cdot}CH(OMe){\cdot}CHBrMe$,

forms large crystals melting at 111°; the corresponding *ethoxy*-derivative crystallises in plates melting at 89°. The *propenyl ether* of *iso*safrole, $CH_2O_2{:}C_6H_3{\cdot}C(OEt){:}CHMe$, prepared by the action of alcoholic alkali hydroxides on β-bromo-α-hydroxydihydro*iso*safrole, boils at 143—145° under 10 mm. pressure. *β-Bromo-α-hydroxydihydro*iso*safrole* and the corresponding dibromosafrole, prepared by heating the corresponding dibromides with calcium carbonate and acetone, could only be obtained as oils. Similarly, by the action of sodium acetate in acetic acid solution on the dibromides, *β-bromo-α-acetoxydihydro*iso*safrole* was obtained as a viscid oil, *β-?-tribromo-α-acetoxydihydro*iso*safrole* forming a colourless, crystalline compound melting at 140—142°.

β-Bromo-α-acetoxypropylbenzene, $OAc{\cdot}CHPh{\cdot}CHBrMe$, is a colourless oil boiling at 142—145° under 11 mm. pressure and having a sp. gr. 1·388 at 19·5°.

*Bromo*iso*safrole dibromide*, $CH_2O_2{:}C_6H_2Br{\cdot}CH{:}CBrMe$, formed by the action of sodium methoxide on bromo*iso*safrole dibromide, melts at 65°. By the action of alcoholic potassium hydroxide on the dibromide, the *allylene* derivative, $CH_2O_2{:}C_6H_2Br{\cdot}C{:}CMe$, melting at 56—59°, is formed. By the action of sodium methoxide on dibromo*iso*safrole dibromide, a *compound*, $CH_2O_2{:}C_6HBr_2{\cdot}CH{:}CBrMe$, melting at 153—154° is formed. The *allylene* derivative,

$CH_2O_2{:}C_6HBr_2{\cdot}C{:}CMe$,

crystallises in colourless needles melting at 180—181°. In carbon disulphide solution, it unites with two atoms of bromine, forming a *compound* melting at 126—128°. E. F. A.

Dibromides of Aromatic Propenyl Compounds. V. Oxides of Propenyl Compounds and their Reactions. PAUL HOERING (*Ber.*, 1905, 38, 3477—3486. Compare preceding abstracts).—Anethole oxide (this vol., i, 593) has a sp. gr. 1·0637 at 17°. Anisylacetone, $OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO{\cdot}CH_3$, has a sp. gr. 1·0707 at 17°; it yields two isomeric *oximes* crystallising in long, colourless needles and melting at 61—62° and 78—79° respectively.

*iso*Safrole oxide has a sp. gr. 1·2128 at 17°. *Piperonylacetone*, $CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}COMe$, boils at 149—151° under 10 mm. pressure and at 283—284° under 760 mm. pressure. The colourless, almost odourless oil has a sp. gr. 1·2017 at 17·5°; the *oxime* separates in needles melting at 87—88°.

β-Bromoanethole oxide is obtained as an oil boiling between 175° and 185° under 18 mm. pressure. *Bromo*iso*safrole β-ketone* yields two isomeric oximes melting at 147—149° and 95° respectively. Dibromo*iso*safrole ketone forms a poorly-defined *oxime* melting at 144—150°.

Both *iso*safrole oxide and bromo*iso*safrole oxide form liquid additive compounds with 1 mol. of acetic acid; the *bromo*iso*safrole glycol*, $CH_2O_2{:}C_6H_2Br{\cdot}CH(OH){\cdot}CHMe{\cdot}OH$, obtained by the action of alcoholic alkali hydroxide on the latter, forms a crystalline compound melting at 107—109°. *Dibromo*iso*safrole glycol β-acetate*, prepared by warming dibromo*iso*safrole oxide with acetic acid, melts at 186—190°; the corresponding *glycol* forms pale yellow plates melting at 154—155°.

β-??-Tribromo-α-hydroxydihydro*iso*safrole forms a *chlorobromide*, $CH_2O_2{:}C_6HBr_2{\cdot}CHCl{\cdot}CHBrMe$, melting at 105—107°. *α-?-Dibromo*iso*safrole β-acetate*, $CH_2O_2{:}C_6H_2Br{\cdot}CHBr{\cdot}CHMe{\cdot}OAc$, prepared either by heating bromo*iso*safrole glycol β-acetate with hydrogen bromide or by the addition of acetyl bromide to bromo*iso*safrole oxide, separates from petroleum in colourless crystals melting at 128—132°; the corresponding *tribromo*iso*safrole-β-acetate* melts at 128—130°.

By the action of hydrogen bromide on *iso*safrole oxide in benzene solution, a colourless, crystalline *compound*, $C_{20}H_{18}O_5$, melting at 240—241°, was obtained. From bromo*iso*safrole oxide, *α-?-dibromo-β-hydroxydihydro*iso*safrole*, a clear, viscid oil which rapidly decomposed, was obtained. *α-?-Dibromo-β-hydroxydihydrodi*iso*safrole*,

$$CH_2O_2{:}C_6HBr_2{\cdot}CH(OH){\cdot}CHBrMe,$$

melts at 121—123°. E. F. A.

p-Hydroxydeoxybenzoin. SIEGMUND WEISL (*Monatsh.*, 1905, **26**, 977—1002. Nencki, Abstr., 1881, 591, 811; Rasinski, Abstr., 1882, 1288).—*p*-Hydroxydeoxybenzoin, $CH_2Ph{\cdot}CO{\cdot}C_6H_4{\cdot}OH$, can be prepared by adding zinc chloride to a boiling mixture of phenylacetic acid and phenol and heating at 170—200°, or by the action of aluminium chloride on phenylacetyl chloride and phenol in nitrobenzene solution at 80° (compare Graebe and Bungener, Abstr., 1879, 790; Behn, D.R.-P. 95901). It crystallises from water in yellowish-red, feathery aggregates, melts at 142° (corr.), is easily soluble in glacial acetic acid, alcohol, ether, benzene, or aqueous alkali hydroxide, but only sparingly so in hot water, and gives a characteristic, dark brown coloration with aqueous-alcoholic ferric chloride. The *acetyl* derivative,

$$CH_2Ph{\cdot}CO{\cdot}C_6H_4{\cdot}OAc,$$

crystallises from dilute alcohol in small, slightly yellow plates and melts at 82° (corr.). The *oxime*, $C_{14}H_{13}O_2N$, formed by Meyer and Oelkers' method (Abstr., 1888, 703), separates from its aqueous-alcoholic solution in glistening, yellowish-white crystals and melts at 85° (corr.).

When boiled with 70 per cent. aqueous potassium hydroxide, *p*-hydroxydeoxybenzoin is decomposed with formation of toluene and *p*-hydroxybenzoic acid.

p-*Hydroxybenzil*, $OH{\cdot}C_6H_4{\cdot}CO{\cdot}COPh$, is formed by oxidation of *p*-hydroxydeoxybenzoin with chromic acid in boiling glacial acetic acid

solution, crystallises slowly from its cold concentrated alcoholic solution, to which water has been added, in small, orange needles, and melts at 175° (corr.). With solid potassium hydroxide in concentrated alcoholic solution, it gives a dark red coloration, which disappears on warming.

The *hydrochloride* of the *dioxime*, $C_{14}H_{12}O_3N_2,2HCl$, crystallises from absolute alcohol in white, prismatic needles and melts and decomposes at 155° (corr.).

When reduced with sodium amalgam in boiling alcoholic solution, *p*-hydroxydeoxybenzoin yields a *product* which has the empirical formula $C_{29}H_{27}O_3$, crystallises from alcohol in small leaflets, and melts at 165° (corr.).

The action of bromine on *p*-hydroxydeoxybenzoin in glacial acetic acid solution leads to the formation of the *bromo*-derivative,

$$OH\cdot C_6H_4\cdot CO\cdot CHPhBr,$$

which crystallises from dilute alcohol, melts at 108° (corr.), and forms silver bromide when treated with silver nitrate in cold aqueous-alcoholic solution. The *iodo*-derivative, $OH\cdot C_6H_4\cdot CO\cdot CHPhI$, formed by adding a solution of iodine in potassium iodide to a boiling aqueous solution of *p*-hydroxydeoxybenzoin and borax, crystallises slowly from alcohol in aggregates of rose-coloured, glistening needles, melts at 195° (corr.), and is easily soluble in warm alcohol, ether, or glacial acetic acid.

Phenyl phenylacetate, $CH_2Ph\cdot CO_2Ph$, is prepared by treating a mixture of phenylacetic acid and phenol with phosphoric oxide in boiling chloroform solution. It is obtained on evaporation of its ethereal solution in nodular aggregates of white crystals, melts at 35° (corr.), and is easily soluble in alcohol, glacial acetic acid, or light petroleum. When boiled with aqueous potassium hydroxide of sp. gr. 1·2, the ester is hydrolysed with formation of phenylacetic acid and phenol.

G. Y.

p-**Hydroxymethyldeoxybenzoins.** EDMUND BLAU (*Monatsh.*, 1905, **26**, 1149—1164).—*4-Hydroxy-3-methyldeoxybenzoin*,

$$CH_2Ph\cdot CO\cdot C_6H_3Me\cdot OH,$$

is formed by adding zinc chloride to a mixture of phenylacetic acid and *o*-cresol heated at 180—200° in a reflux apparatus or by the action of aluminium chloride on phenylacetyl chloride and *o*-cresol dissolved in nitrobenzene. It crystallises from hot water in slightly yellow or red, feathery, crystalline aggregates, melts at 152°, is easily soluble in aqueous alkali hydroxides, alcohol, ether, or benzene, and gives a characteristic brown coloration with aqueous ferric chloride. When boiled with 70 per cent. aqueous potassium hydroxide in a reflux apparatus, it is decomposed with formation of toluene and 6-hydroxy-*m*-toluic acid. The *acetyl* derivative, $CH_2Ph\cdot CH_2\cdot CO\cdot C_6H_3Me\cdot OAc$, crystallises from dilute alcohol in glistening, white needles and melts at 73°. The *oxime*, $C_{15}H_{14}O\colon N\cdot OH$, crystallises in quadratic leaflets or white needles and melts at 158°.

4-Hydroxy-3-methylbenzil, $CH_2Ph\cdot CO\cdot CO\cdot C_6H_3Me\cdot OH$, is formed by the oxidation of 4-hydroxy-3-methyldeoxybenzoin with chromic oxide in

boiling glacial acetic acid solution; it separates from dilute acetic acid as a yellow, flocculent precipitate, melts at 182—183°, or when boiled with water, and gives a dark red coloration with potassium hydroxide in alcoholic solution. The *hydrochloride* of the *dioxime*,

$$C_{15}H_{14}O_3N_2,2HCl,$$

crystallises from alcohol in long, white needles and melts at 149°.

When reduced with sodium amalgam in alcoholic solution, 4-hydroxy-3-methyldeoxybenzoin yields a *product*, $C_{31}H_{32}O_3$, which separates from alcohol as a white, flocculent precipitate and melts at 117°. *Bromo-4-hydroxy-3-methyldeoxybenzoin*, $C_{15}H_{13}O_2Br$, is formed by the action of bromine on 4-hydroxy-3 methyldeoxybenzoin in glacial acetic acid solution at 80°; it crystallises from dilute alcohol and melts at 132°. *Iodo-4-hydroxy-3-methyldeoxybenzoin*, $C_1\ H_{13}O_2I$, formed by the action of iodine in potassium iodide solution on 4-hydroxy-3-methyldeoxybenzoin in presence of sodium borate, crystallises in concentric aggregates of glistening needles and melts at 120°. These bromo- and iodo-compounds yield the silver haloids when treated with silver nitrate in aqueous-alcoholic solution.

4-*Hydroxy-2-methyldeoxybenzoin*, $CH_2Ph\cdot CO\cdot C_6H_3Me\cdot OH$, is formed by the condensation of *m*-cresol and phenylacetic acid in presence of zinc chloride at 200°; it melts at 142°, is soluble in hot water, alcohol, or glacial acetic acid, and yields toluene and 4-hydroxy-*o*-toluic acid when boiled with 70 per cent. aqueous potassium hydroxide.

G. Y.

Dihydroxydeoxybenzoins. Friedrich Finzi (*Monatsh.*, 1905, 26, 1119—1138. Compare Bülow and Grotowsky, Abstr., 1902, i, 554).—1-*m*-Dihydroxydeoxybenzoin (dihydroxyphenyl benzyl ketone), $C_6H_3(OH)_2\cdot CO\cdot CH_2Ph$ [$(OH)_2 = 2:4$ or $2:6$], is formed by heating phenylacetic acid and resorcinol in molecular amounts, with zinc chloride, not above 150°, or by adding aluminium chloride to a solution of molecular amounts of phenylacetyl chloride and resorcinol in nitrobenzene at 70—80°. It crystallises from much boiling water in thin, glistening leaflets, melts at 104° (corr.), is soluble in most organic solvents, aqueous alkali hydroxides, or, without evolution of carbon dioxide, in sodium carbonate solution, and with ferric chloride in aqueous or alcoholic solution gives a dark violet coloration, which disappears on addition of sodium carbonate. It is identical, probably, with Bülow and Grotowsky's product (*loc. cit.*). When treated with acetyl chloride in pyridine solution, dihydroxydeoxybenzoin forms the *diacetyl* derivative, $C_{14}H_{10}O_3Ac_2$, which crystallises from alcohol in slender, white needles, melts at 107° (corr.), and is easily soluble in concentrated sulphuric acid, acetone, chloroform, or benzene at the laboratory temperature. The *oxime*, $C_{14}H_{12}O_2{:}N\cdot OH$, crystallises in slender, yellow needles, sinters at 110°, and melts partially at 170°.

1-m-*Dihydroxybenzil*, $C_6H_3(OH)_2\cdot CO\cdot COPh$ [$(OH)_2 = 2:4$ or $2:6$], is obtained in a yield of 15 per cent. of the theoretical by oxidising dihydroxydeoxybenzoin with an excess of potassium permanganate in dilute aqueous alkali carbonate solution, or in an almost theoretical yield by oxidation with boiling Fehling's solution. On addition to water of its solution in glacial acetic acid, it separates as a brown,

amorphous substance which sinters at 137°, melts at 239°, and is insoluble in water or light petroleum, but dissolves readily in alcohol, ether, or glacial acetic acid. The *hydrochloride* of the *dioxime*, $C_{14}H_{12}O_4N_2,2HCl$, crystallises in long, colourless needles and melts at 155—156°.

Reduction of 1-*m*-dihydroxydeoxybenzoin, by means of sodium amalgam in boiling alcoholic solution through which a current of carbon dioxide is passed, leads to the formation of an amorphous, brown *product*, $C_{22}H_{18}O_4$, which is easily soluble in alcohol, ether, or acetone.

3 : 4-*Dihydroxydeoxybenzoin* (3 : 4-*dihydroxyphenyl benzyl ketone*), formed by adding zinc chloride to a mixture of phenylacetic acid and catechol at 140—150°, or by the action of aluminium chloride on a mixture of phenylacetyl chloride and catechol, crystallises from water in small, brown needles, melts at 173°, and with alcoholic ferric chloride gives a green coloration which becomes violet on addition of ammonia. When heated with 70 per cent. aqueous potassium hydroxide at 180°, it is decomposed with formation of toluene and 3 : 4-dihydroxybenzoic acid. The *diacetyl* derivative, $C_{18}H_{16}O_7$, crystallises from aqueous alcohol in glistening, white needles and melts at 105° (corr.).

2 : 5-*Dihydroxydeoxybenzoin* (2 : 5-*dihydroxyphenyl benzyl ketone*), formed by heating phenylacetic acid and quinol with zinc chloride at 150°, or by the action of aluminium chloride on a mixture of phenylacetyl chloride and quinol, crystallises in needles and melts at 170°. G. Y.

Certain Derivatives of Tetrabromo-*o*-benzoquinone. C. Loring Jackson and H. A. Carlton (*Amer. Chem. J.*, 1905, **34**, 422—441. Compare Jackson and Porter, Abstr., 1904, i, 254).—The red compound, $4C_6O_2Br_4,MeOH$, formed as the first product of the action of methyl alcohol on tetrabromo-*o*-benzoquinone, can also be obtained by the action of tetrabromo-*o*-benzoquinone on the α-compound, $2C_6O_2Br_4,MeOH$. When either the red compound or the α-compound is warmed with dilute sodium hydroxide, the β-compound,

$$2C_6O_2Br_4,MeOH,$$

is produced. By similar treatment, the α-benzyl compound is converted into the corresponding β-compound.

Both α- and β-compounds have been obtained with ethyl alcohol, *n*-propyl alcohol, and *iso*amyl alcohol. The following is a list of these compounds with their decomposition or melting points : $2C_6O_2Br_4,EtOH$, *α-compound*, 180—185°, *β-compound*, 228° ; $2C_6O_2Br_4,Pr^aOH$, *α-compound*, 180°, *β-compound*, 176° ; $2C_6O_2Br_4,C_5H_{11}\cdot OH$, *α-compound*, 150°, *β-compound*, 177° ; $2C_6O_2Br_4,CH_2Ph\cdot OH$, *α-compound*, 165—170°, *β-compound*, 216—217°. The α-*iso*amyl compound melts without becoming red, but when heated to 190° it is converted, like the other α-compounds, into hexabromo-*o*-quinocatechol ether. *tert.*-Butyl alcohol also appears to yield an α-compound, but the product was not obtained in the pure state.

When the water, methyl alcohol, and benzyl alcohol α-compounds are reduced with zinc and acetic acid, they all yield the same product

melting at 274—275°. This compound has not the composition assigned to it by Jackson and Porter (*loc. cit.*), but is probably represented by the formula $C_6Br_4{:}O_2{:}C_6H(OH)_2O{\cdot}C_6Br_4{\cdot}OH$; its *diacetyl* derivative melts at 304—305°, and its triacetyl derivative melts at 273—275°; the *tribenzoyl* derivative melts at 250—255°. When this reduction product is treated with nitric acid, it is converted into a mixture of two *substances*, one of which crystallises in small, red prisms and melts at 275—280°, whilst the other forms orange needles and does not melt below 310°. If the crude reduction product is boiled with alcohol or benzene, a *substance* is produced which has a pale lilac colour, becomes brown at about 200°, and does not melt below 310°; this substance cannot be obtained from the pure reduction product.

The *acetyl* derivative of the benzyl alcohol β-compound, $2C_6O_2Br_4,CH_2Ph{\cdot}OAc$, crystallises in small, white needles and melts at 210°. If the action of acetic anhydride is continued for six hours, a dark, charred mass is obtained, from which a mixture of benzene and methyl alcohol extracts a *substance* crystallising in brown needles and melting at 190—195°. E. G.

Additive Compounds of Quinones and Tertiary Amines. C. LORING JACKSON and LATHAM CLARKE (*Amer. Chem. J.*, 1905, **34**, 441—459).—By the action of dimethylaniline on quinones, unstable additive compounds are produced. The following compounds have been prepared. The additive *compound* of tetrabromo-*o*-quinone, $C_6O_2Br_4,C_6H_5{\cdot}NMe_2$, forms lustrous, purple needles which undergo rapid decomposition. Tetrachloro-*o*-benzoquinone yields a similar but even less stable product. Tetrachloro-*p*-benzoquinone yields a *compound*, $C_6O_2Cl_4,C_6H_5{\cdot}NMe_2$, which crystallises in slender, deep blue prisms, melts at 105°, and decomposes rapidly on exposure to the air; when heated above its melting point, it is converted into the dark blue substance first described by Greiff (Abstr., 1880, 41). Trichloro-*p*-benzoquinone furnishes a *compound*, $C_6HO_2Cl_3,C_6H_5{\cdot}NMe_2$, which crystallises in slender, dark blue prisms, melts at 65°, and is soluble in ether, benzene, or acetone. The additive *compound* with 2 : 5-dichloro-*p*-benzoquinone crystallises in slender, deep blue needles. Chloroquinone and quinone yield dark red products with dimethylaniline from which a solid substance could not be isolated. The additive compound of tetrabromo-*p*-benzoquinone, $C_6O_2Br_4,C_6H_5{\cdot}NMe_2$, forms purple, microscopic needles and melts at 65—68°. Trichlorotoluquinone gives a *compound*, $C_6MeO_2Cl_3,C_6H_5{\cdot}NMe_2$, which crystallises in flat, purple prisms, melts at 68—73°, and is soluble in alcohol, benzene, or acetone. Toluquinone, dibromothymoquinone, dichlorodiethoxyquinone, 1 : 4-naphthaquinone and anthraquinone were found to unite with dimethylaniline to form coloured products from which no solid substance could be isolated. Quinone dibromide and quinone tetrabromide give a blue coloration with dimethylaniline. *p*-Quinoneoxime and 2 : 5-dichloroquinoneoxime give a red coloration with dimethylaniline, but the corresponding dioximes yield no coloration. The following compounds give no change of colour when treated with dimethylaniline. *p*-Diketo*cyclo*hexene, dichlorodimethoxyquinone

dibenzoyldimethylacetal, dichlorodiethoxyquinone tetraethylacetal, dichlorodi*iso*amyloxyquinone, dichlorcdiphenoxyquinone, dianilinobromoquinoneanil, tetrachloroquinol, dichlorodi*iso*amyloxyquinol, and dichlorodibenzyloxyquinol.

Coloured products are formed by the action of *p*-bromodimethylaniline and of dibromodimethylaniline on quinone and trichloroquinone. The hydrobromide of dibromodimethylaniline gives a slight red coloration with trichloroquinone due to partial dissociation of the salt. Neither phenyltrimethylammonium bromide nor iodide gives any coloration with quinone or trichloroquinone.

The additive *compound*, $C_6O_2Cl_4,C_6H_4Me\cdot NMe_2$, obtained by the union of tetrachloro-*p*-benzoquinone and dimethyl-*p*-toluidine, forms blue crystals, melts at 114°, is sparingly soluble in alcohol or acetone, and is unstable in the air. The *compound*, $C_6HO_2Cl_3,C_6H_4Me\cdot NMe_2$, from trichloroquinone and dimethyl-*p*-toluidine, crystallises in long, blue needles. Coloured products are also formed by the action of dimethyl-*p*-toluidine on 2 : 5-dichloroquinone, chloroquinone, and quinone. The additive *compound*, $C_6MeO_2Cl_3,C_6H_4Me\cdot NMe_2$, from trichlorotoluquinone and dimethyl-*p*-toluidine, crystallises in deep blue needles and melts at 74—76°. The *compound*,

$$C_6O_2Br_4,C_6H_4Me\cdot NMe_2,$$

from tetrabromo-*p*-benzoquinone, forms pale blue crystals and melts at 109°.

The action of dimethyl-*o*-toluidine, benzyldimethylamine, dimethyl*iso*amylamine, α-naphthyldimethylamine, α-naphthyldiethylamine, β-naphthyldiethylamine, α-naphthylamine, diphenylamine, pyridine, methylaniline, and tetramethyldiaminotriphenylmethane on various quinones has been studied and the results are described; in every case a coloured product is obtained.

The probable constitution of these additive compounds is discussed.

E. G.

Preparation of 2-Hydroxy-1 : 4-naphthaquinone. HERBERT TEICHNER and HUGO WEIL (*Ber.*, 1905, 38, 3376—3377).—2-Hydroxy-1 : 4-naphthaquinone is easily prepared by adding a cold mixture of hydrogen peroxide and aqueous sodium hydroxide to 1 : 2-naphthaquinone suspended in water. Sodium 1 : 2-naphthaquinone-6-sulphonate is oxidised in a similar manner to sodium 2-hydroxy-1 : 4-naphthaquinone-6-sulphonate; but sodium 1 : 2-naphthaquinone-3 : 6-disulphonate cannot be converted into the corresponding derivative of α-naphthaquinone.

W. A. D.

Condensations with 1 : 2-Naphthaquinone-4-sulphonic Acid. FRANZ SACHS and MARIO CRAVERI (*Ber.*, 1905, 38, 3685—3696. Compare Ehrlich and Herter, Abstr., 1904, i, 598).—2-*Hydroxy*-1 : 4-*naphthaquinone*-4-*phenylcyanomethide*, $CO<\substack{C(OH):CH \\ C_6H_4}>C:CPh\cdot CN$, prepared by the interaction of sodium naphthaquinone sulphonate with benzyl cyanide, crystallises in yellow needles melting at 201° and gives a red coloration with alcoholic sodium hydroxide, the solution in concentrated

sulphuric acid being dark violet. The *phenylhydrazone*,

$$N_2HPh:C<\begin{matrix}C(OH):CH\\ C_6H_4\end{matrix}>C:CPh\cdot CN,$$

crystallises in cherry-red leaflets melting at 250°; it gives with sulphuric acid a dark cherry-red, and with alkaline hydroxides an orange-yellow coloration. The *ethyl ether*, $OEt\cdot C_{10}H_5O:CPh\cdot CN$, separates in yellow rods melting at 163—165°; the *methyl ether* forms yellow needles, which melt at 190°. *2-Methoxy-4-cyanobenzyl-α-naphthol*, $OH\cdot C_{10}H_5(OMe)\cdot CHPh\cdot CN$, prepared by reducing the methyl ether with zinc dust and acetic acid, crystallises in colourless, star-shaped needles or prisms melting at 195°; the *acetate* separates in colourless prisms and melts at 167—168°.

1 : 2-*Diacetoxy-4-cyanobenzylnaphthalene*, $C_{10}H_5(OAc)_2\cdot CHPh\cdot CN$, formed by the direct reduction of the hydroxynaphthaquinone with zinc dust and acetic acid in presence of sodium acetate and acetic anhydride, forms colourless prisms melting at 153—155°.

4-*Cyanobenzyl*-1 : 2-*naphthaquinol*, $C_{10}H_5(OH)_2\cdot CHPh\cdot CN$, is obtained in the form of colourless, narrow plates or rhombic cubes melting at 235°. When condensed with *o*-phenylenediamine, hydroxynaphthaquinonephenylcyanomethide yields a *compound* melting at 228° and crystallising in light yellow needles, which dissolve in sulphuric acid with a dark bordeaux-red and in alcoholic alkaline hydroxides with a green coloration.

2-*Hydroxy*-1 : 4-*naphthaquinone*-4-p-*nitrophenylcyanomethide*, prepared from *p*-nitrobenzyl cyanide and the sulphonic acid, is a yellow powder melting at 220° and possessing electrical properties; the *methyl ether* crystallises in yellow rods or needles melting at 243°, whilst the condensation product with *o*-phenylenediamine separates in greenish-yellow rods, which melt at 212—214° and dissolve in alcoholic alkali hydroxides with a blue coloration.

2-Hydroxy-1 : 4-naphthaquinone-4-dicarbethoxymethide,

$$OH\cdot C_{10}H_5O:C(CO_2Et)_2,$$

obtained on condensing the sulphonate with ethyl malonate, crystallises in thick, yellow needles melting at 110—112°, and is identical with the compound described by Liebermann (Abstr., 1899, i, 373).

Ethyl 2-*hydroxy*-1 : 4-*naphthaquinone*-4-*cyanomethidecarboxylate*,

$$OH\cdot C_{10}H_5O:C(CN)\cdot CO_2Et,$$

crystallises in yellow rods melting at 130° and gives a reddish-yellow coloration with sulphuric acid. The *oxime* crystallises in brownish-yellow rods melting at 236°. With *o*-phenylenediamine, a *compound*, $C_{21}H_{15}O_2N_3$, is obtained which melts at 156—159° and crystallises in small, yellow bundles of needles. 2-*Hydroxy*-1 : 4-*naphthaquinone*-4-*dicyanomethide* forms yellow needles, melting at 213°, and gives a dark reddish-yellow solution in sulphuric acid. E. F. A

2-Bromo-α-aminoanthraquinone. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 160169).—Finely-divided α-aminoanthraquinone, prepared by precipitating its solution in sulphuric acid with water, is suspended in glacial acetic acid and the calculated quantity of bromine added. After boiling and again cooling, 2-*bromo-α-aminoanthraquinone* separates in rosettes of yellowish-red needles. It melts at 180—181°

and is insoluble in water, but dissolves readily in hot glacial acetic acid, aniline, or pyridine, sparingly in alcohol or ether. The solution in concentrated sulphuric acid is yellow, that in acid containing 40 per cent. anhydride is bluish-violet.

2-*Bromo*-5-*nitro*-α-*aminoanthraquinone*, prepared in similar manner from 5-nitro-α-aminoanthraquinone, forms reddish-brown needles and melts at 240—245°. C. H. D.

Elimination of the Sulpho-group from Anthraquinone Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 160104. Compare Abstr., 1904, i, 513; this vol., i, 361).—It has been shown that the sulphonation of anthraquinone and its derivatives in the α-position takes place most readily in the presence of a mercury salt. It is now found that the elimination of the α-sulpho-group, which is only incomplete on heating with dilute sulphuric acid, is rendered complete by the addition of a mercury salt. In this way, anthraquinone is obtained from either anthraquinone-α-sulphonic acid or anthraquinone-1 : 5- or -1 : 8-disulphonic acid. C. H. D.

Chrysophanic Acid. OTTO A. OESTERLE (*Arch. Pharm.*, 1905, **243**, 434—442).—Chrysophanic acid was prepared from chrysarobin by oxidation in alkaline solution and fractional crystallisation from benzene. The fraction of highest melting point melted at 186° and still contained methoxyl; it was freed from methoxyl by heating it in benzene solution with aluminium chloride (hydriodic acid effects reduction to the hydroanthranone at the same time that it removes methoxyl). *Chrysophanic acid*, $C_{15}H_{10}O_4 = C_{15}H_8O_2(OH)_2$, when free from methoxyl, crystallises in brownish-yellow plates which melt at 196°; its pale yellow *diacetyl* derivative melts at 208°.

Chrysophanic acid cannot be methylated with methyl iodide. But when a solution of the crude acid in aqueous potassium hydroxide is shaken with methyl sulphate, and the solid which separates is extracted with boiling dilute aqueous sodium hydroxide, the insoluble residue contains the *dimethyl ether* of chrysophanic acid, $C_{15}H_8O_2(OMe)_2$, which crystallises in orange-yellow needles melting at 195°, mixed with a small quantity of another yellow substance melting at 224° (probably a trimethoxymethylanthraquinone), which lowers its melting point and is very difficult to separate from it. The alkaline extract contains unchanged chrysophanic acid together with its *monomethyl ether*; the latter can be precipitated by saturating the solution with carbon dioxide; it crystallises in orange needles, which melt at 204° and form a lemon-yellow *acetyl* derivative melting at 204—205°. C. F. B.

Resin Oil of Pinus Longifolia. FRANK RABAK (*Chem. Centr.*, 1905, ii, 896—897; from *Pharm. Rev.*, 23, 229—232).—The resin oil prepared from *Pinus longifolia*, which is indigenous to the lower Himalayas, forms a white, rather tough, opaque mass and has a granular structure which is probably due to partial crystallisation of the resin acid. Its odour is extremely pleasant and somewhat resembles that of limonene. It has a sp. gr. 0·990, $[\alpha]_D$ −7°42′, acid number 129, ester number 11, and saponification number 140. When distilled with steam it yields about 18·5 per cent. of a volatile oil which has the characteristic odour

of pinene and a somewhat fainter odour of limonene. The oil has a sp. gr. 0·866 and $[\alpha]_D$ +2°48′. When fractionally distilled, it yields (1) 56 per cent. of a liquid which boils at 165—170° and has $[\alpha]_D$ −2°; (2) 20 per cent. which boils at 170—175° and has $[\alpha]_D$ +2°48′; (3) 9 per cent. which boils at 175—180° and has $[\alpha]_D$ +6°50′; and (4) 15 per cent. which boils at 180° and above and has $[\alpha]_D$ +18°12′. The oil probably contains *l*-pinene together with a small quantity of *d*-limonene. The presence of pinene was detected in the first fraction by means of amyl nitrite, but a crystalline nitrosochloride was not isolated. Attempts to prepare the hydrochloride and bromine additive compound also failed. The white, crumbly resin which remains after distilling the oil has acid number 142, ester number 13, and saponification number 155; a 10 per cent. solution in a 100 mm. tube has α_D = 1°10′. Crystals of a resin acid melting at 138—140° separate from the solution of the resin in glacial acetic acid after remaining for 24 hours.

E. W. W.

The Cyanogenetic Glucosides in the Leaves of the Cherry-laurel (Prunus Laurocerasus) and in the Bark of the Bird-cherry (P. Padus). KARL JOUCK (*Arch. Pharm.*, 1905, **243**, 421—426).—A yellow, amorphous, very hygroscopic *glucoside* was isolated from the bark of *Prunus padus* by a method described in detail in the paper, the yield being 0·5 per cent. It contained C 53·6, H 6·8, N 2·84 per cent.; it yielded 6·1 per cent. of hydrocyanic acid and 38·9 of dextrose when hydrolysed with emulsin, and an *acid* was obtained from it analogous with amygdalic acid and forming a *barium* salt which contained C 40·5, H 5·6, Ba 16·5 per cent.

From the leaves of *P. laurocerasus*, a similar *glucoside* was isolated in a similar manner; the yield was 0·8 per cent. It contained C 54·3, H 6·8, N 1·54 per cent.; it yielded 2·75 per cent. of hydrocyanic acid and 27·2 of dextrose when hydrolysed, and the crystalline *barium* salt of the *acid* obtained from it analogous to amygdalic acid contained C 42·1, H 5·4, Ba 14·2 per cent.

C. F. B.

Sambunigrin, a New Cyanogenetic Glucoside obtained from the Leaves of Sambucus Nigra. ÉMILE BOURQUELOT and ÉMILE DANJOU (*Compt. rend.*, 1905, **141**, 598—600; *J. Pharm. Chim.*, [vi], **22**, 385—391. Compare this vol., ii, 605, and Guignard, this vol., ii, 604).—The leaves of *Sambucus nigra* contain only traces of emulsin; it is therefore possible to extract from the air-dried or the fresh leaves the glucoside *sambunigrin*, $C_{14}H_{17}O_6N$, which crystallises from ethyl acetate in long, colourless needles, sinters at 149°, and melts at 151—152°, has $[\alpha]_D$ −76·3°, is readily soluble in water or ethyl alcohol, less soluble in ethyl acetate, and almost insoluble in ethyl ether; it has a sweet taste at first, afterwards becoming bitter. On hydrolysis by means of emulsin, sambunigrin yields dextrose, hydrogen cyanide, and benzaldehyde, and is therefore an isomeride of Fischer's amygdonitrile glucoside, $C_{14}H_7O_6N$, from which it differs by its strong lævorotatory power −76·3° instead of −26·1°.

M. A. W.

Aloes. ALEXANDER TSCHIRCH and O. HOFFBAUER (*Arch. Pharm.*, 1905, **243**, 399—420).—From Zanzibar aloes, an *aloin* could not be obtained satisfactorily by means of lime or of chloroform and methyl alcohol. It was found best to allow the powdered drug to remain for several days with an equal weight of alcohol, the mixture being shaken occasionally, and then to recrystallise the insoluble portion (zanaloin) from dilute alcohol. *iso*Aloin is not present. From Jaferabad, Barbadoes, and Curaçoa aloes, the aloins (jafaloin, barbaloin, and curaloin) could be obtained by extracting with methyl alcohol and freeing the extract from resin by precipitation with chloroform. Barbaloin and curaloin are identical, with melting point 147° and composition $C_{16}H_{16}O_7$. Capaloin, from *Aloe lucada*, and the aloin of the Uganda aloe are also identical, with melting point 147° but composition $C_{16}H_{18}O_7$; zanaloin also has this composition, but melts at 212°. Jafaloin, melting at 152° and containing C 60·5, H 5·5 per cent., and nataloin are distinct individuals. The aloes from the Barbadoes contained but little *iso*aloin, and those from Jaferabad contained none, whilst those from Curaçoa contained a considerable quantity.

Aloin-reds were isolated from Natal and Curaçoa aloes, in very small amount in the latter case. The former has the composition, $C_{16}H_{16}O_8$, of an oxidation product of nataloin; it does not yield chrysamic acid when heated with concentrated nitric acid, whereas curaloin-red does. The solubilities and absorption spectra of several aloin-reds are described.

From Curaçoa aloes, an *anthraglucoside* was isolated, which, by boiling with 1 per cent. sulphuric acid, was hydrolysed to emodin and a sugar, of which the phenylosazone melted at 183° (compare Leger, Abstr., 1904, i, 907).

When hydrolysed with boiling 10 per cent. sulphuric acid, the *resin* of Zanzibar aloes yields *p*-coumaric acid, and that of Curaçoa aloes cinnamic acid, whilst the corresponding acid product from Jaferabad aloes could not be isolated; in all cases, a *resinotannol* was obtained also. All these resinotannols yield picric and oxalic acids when heated with nitric acid of sp. gr. 1·27. Barb- and cur-aloresinotannols have the composition $C_{22}H_{26}O_6$; zanaloresinotannol is $C_{22}H_{22}O_8$, isomeric with cap- and nat-aloresinotannol; whilst jafaloresinotannol is $C_{20}H_{18}O_6$, isomeric with feroaloresinotannol. Accompanying jafaloresinotannol is a substance which is soluble in water and yields a little chrysamic acid when oxidised with nitric acid. C. F. B.

Red Sulphur-Dyes from Resorcinol. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 160395).—Red dyes are obtained when resorcinol is fused with sulphur and an aromatic formyl compound such as formanilide, with or without the addition of glycerol as a solvent, at 180—185°. The products are dark red, insoluble in water, and dissolve in sodium sulphide to red solutions. C. H. D.

Yellow Sulphur Dye. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 159725).—A fast yellow die, soluble in sodium sulphide, is obtained on fusing 2:4-diaminophenyl thiocyanate with sulphur at 140—240°. C. H. D.

Constitution of Tannin. MAXIMILIAN NIERENSTEIN (*Ber.*, 1905, **38**, 3641—3642).—In agreement with the usual supposition that tannin is a digallic acid, $C_6H_2(OH)_3 \cdot CO \cdot O \cdot C_6H_2(OH)_2 \cdot CO_2H$, it is shown that when distilled with zinc dust it yields diphenylmethane, just as compounds of the type $\begin{matrix} C_6H_4 \cdot CO \\ | \quad\quad | \\ C_6H_4 \cdot O \end{matrix}$ yield fluoran (Graebe, Abstr., 1903, i, 262; A. G. Perkin and Nierenstein, Trans., 1905, **87**, 1412). J. J. S.

Bromo-derivatives of 4-Pyrone and the Stability of Halogen Derivatives of 2- and 4-Pyrones. FRANZ FEIST and ERICH BAUM (*Ber.*, 1905, **38**, 3562—3574. Compare Feist, Abstr., 1892, 587; 1893, i, 403; Feist and Molz, Abstr., 1899, i, 675; Peratoner and Castellana, this vol., i, 806; Peratoner and Tamburello, *ibid.*, 807).—The action of a large excess of bromine on 4-pyrone in presence of a small quantity of iodine, ferric chloride, or phosphorus leads to the formation of a *perbromide*; this is obtained as a yellow, crystalline powder, and when treated with boiling water decomposes with formation of (1) 3 : 5-*dibromo*-4-*pyrone*, $O<\begin{matrix} CH:CBr \\ CH:CBr \end{matrix}>CO$, which crystallises from ether in prisms, or from water or light petroleum in needles, melts at 157·5°, and is only slightly volatile in a current of steam; (2) 3-*bromo*-4-*pyrone*, $O<\begin{matrix} CH:CBr \\ CH=CH \end{matrix}>CO$, which crystallises from light petroleum in prisms, softens at 109°, and melts at 114°; (3) pentabromoacetone, and (4) an *oil* which on treatment with phenylhydrazine forms phenylhydrazine hydrobromide. When treated with ammonia in absolute alcoholic solution, 3 : 5-dibromo-4-pyrone yields only a small quantity of 3 : 5-*dibromopyridone*, $C_5H_3OBr_2N$, which crystallises in silvery leaflets and decomposes at about 300°.

The *perbromide*, formed by the action of an excess of bromine on 2 : 6-dimethyl-4-pyrone in presence of iodine, has approximately the formula $(C_7H_7O_2Br)_2,Br_2,HBr$ (compare Collie and Steele, Trans., 1900, **77**, 1114); it is obtained as a sulphur-yellow powder, does not colour carbon disulphide except in presence of water, liberates iodine from potassium iodide, and when boiled with water evolves bromine and yields bromo- and dibromo-dimethylpyrones, together with a polybromo-derivative of acetone.

3-*Bromo*-2 : 6-*dimethyl*-4-*pyrone*, $O<\begin{matrix} CMe:CBr \\ CMe:CH \end{matrix}>CO$, crystallises from light petroleum in matted, white needles, melts at 75—76°, is easily soluble in water, ether, chloroform, or alcohol, reduces warm Fehling's solution, and, although less basic than 2 : 6-dimethyl-γ-pyrone, forms a *hydrobromide* which is partially decomposed by water and chloroform.

3 : 5-*Dibromo*-2 : 6-*dimethyl*-4-*pyrone*, $O<\begin{matrix} CMe:CBr \\ CMe:CBr \end{matrix}>CO$, crystallises from boiling water or petroleum in slender needles, melts at 163—164°, sublimes partially, is not volatile in a current of steam, does not give a coloration with ferric chloride, and does not reduce

Fehling's solution; when boiled with aqueous barium hydroxide, it becomes slightly yellow, but does not form a yellow xantho-barium salt. When evaporated with aqueous ammonia or treated with ammonia in absolute alcoholic solution, it forms only a small amount of *dibromodimethylpyridone*, $NH<\begin{matrix}CMe:CBr\\CMe:CBr\end{matrix}>CO$, which crystallises in glistening leaflets and melts and decomposes at 291°.

3-*Bromo*-2 : 6-*dimethylpyridone*, $NH<\begin{matrix}CMe:CBr\\CMe:CH\end{matrix}>CO$, formed in small quantity by the action of absolute alcoholic ammonia on 3-bromo-2 : 6-dimethyl-4-pyrone, decomposes at 292°. Bromo- and dibromo-2 : 6-dimethyl-4-pyrones do not yield the corresponding hydroxy- and dihydroxy-derivatives when treated with alkali hydroxides. With aqueous sodium hydroxide, the bromo-compound forms an oil which contains bromine and gives a brownish-red coloration with ferric chloride (compare Collie and Tickle, Trans., 1902, **81**, 1004). When warmed with aqueous potassium hydroxide or calcium carbonate or with alcoholic sodium ethoxide, the dibromo-compound forms a small amount of a *substance*, $C_7H_7O_3Br$, which crystallises in white leaflets, melts at 106°, gives a bluish-red coloration with ferric chloride, and may have the constitution $O<\begin{matrix}CMe=CBr\\CMe:C(OH)\end{matrix}>CO$ or $O<\begin{matrix}CHAc\cdot CO\\CMe=CBr\end{matrix}$.

Ethyl dibromochelidonate, $CO<\begin{matrix}CBr:C(CO_2Et)\\CBr:C(CO_2Et)\end{matrix}>O$, is formed by the action of bromine on ethyl acetonedioxalate; it separates from ether in glistening crystals, melts at 126—127° when heated with concentrated hydrochloric acid, and is decomposed with formation of oxalic acid. G. Y.

Synthesis of Fisetin. STANISLAUS VON KOSTANECKI and S. NITKOWSKI (*Ber.*, 1905, **38**, 3587—3589. Compare Kostanecki, Lampe, and Tambor, Abstr., 1904, i, 441; Perkin, Trans., 1904, **85**, 1459).—When boiled with acetic anhydride and sodium acetate, 2′-hydroxy-3 : 4 : 4′-trimethoxychalkone, obtained by condensation of paeonol with veratraldehyde, forms the *acetyl* derivative,

$$OAc\cdot C_6H_3(OMe)\cdot CO\cdot CH:CH\cdot C_6H_3(OMe)_2,$$

which crystallises from dilute alcohol in yellow needles and melts at 90°. 3 : 3′ : 4′-Trimethoxyflavanone, melting at 120—121°, is obtained by boiling 2′-hydroxy-3 : 4 : 4′-trimethoxychalkone with alcoholic hydrochloric acid in a reflux apparatus. It forms the iso*nitroso*-derivative, $\begin{matrix}C_6H_3(OMe)\cdot O\\CO-C(N\cdot OH)\end{matrix}>CH\cdot C_6H_3(OMe)_2$, which crystallises from benzene in almost white needles, melts and decomposes at 183°, and when boiled with glacial acetic acid and 10 per cent. sulphuric acid is hydrolysed to hydroxylamine and 3 : 3′ : 4′-*trimethoxyflavanol*,

$$\begin{matrix}OMe\cdot C—CH:C—O—C——C:CH—C\cdot OMe\\CH\cdot CH:C\cdot CO\cdot C\cdot OH\ CH:CH\cdot C\cdot OMe\end{matrix}.$$

This crystallises from alcohol in yellow needles, melts at 186°, dissolves in alcohol to form a solution with green fluorescence, and forms a sparingly soluble *sodium* derivative and an *acetyl* derivative,

$C_{15}H_6O_2(OMe)_3{\cdot}OAc$, crystallising in white needles and melting at 170°.

When boiled with concentrated hydriodic acid, 3 : 3′ : 4′-trimethoxyflavanol and its acetyl derivative are converted into fisetin (3 : 3′ : 4′-trihydroxyflavanol). G. Y.

3-Methoxycoumaranone. A. Blom and Josef Tambor (*Ber.*, 1905, **38**, 3589—3592. Compare Feuerstein and Kostanecki, Abstr., 1899, i, 538).—The action of bromoacetyl bromide and aluminium chloride on *m*-dimethoxybenzene in carbon disulphide solution leads to the formation of *a-bromoresacetophenone dimethyl ether*,

$$CH_2Br{\cdot}CO{\cdot}C_6H_3(OMe)_2,$$

which crystallises from dilute alcohol in small, colourless needles, melts at 102°, and when boiled with potassium acetate in absolute alcoholic solution in a reflux apparatus yields *3-methoxycoumaranone*, $OMe{\cdot}C_6H_3{<}^{O}_{CO}{>}CH_2$. This crystallises from alcohol in yellow needles, melts at 125°, dissolves in concentrated sulphuric acid to form a solution which gradually assumes a green fluorescence, and condenses with veratraldehyde in aqueous-alcoholic sodium hydroxide solution to form 3 : 3′ : 4′-*trimethoxybenzylidenecoumaranone*,

$$OMe{\cdot}C_6H_3{<}^{O}_{CO}{>}C{:}CH{\cdot}C_6H_3(OMe)_2,$$

which crystallises from alcohol in slender, glistening, yellow needles and melts at 189° (compare Emilewicz and Kostanecki, Abstr., 1899, i, 368 ; Kostanecki and Rózycki, *ibid.*, 911). It is formed also by the action of hot alcoholic potassium hydroxide on 2′-*acetoxy*-3 : 4 : 4′-*trimethoxychalkone dibromide*,

$$OAc{\cdot}C_6H_3(OMe){\cdot}CO{\cdot}CHBr{\cdot}CHBr{\cdot}C_6H_3(OMe)_2,$$

which is obtained by treating 2′-acetoxy-3 : 4 : 4′-trimethoxychalkone (Kostanecki and Nitkowski, preceding abstract) with bromine in carbon disulphide solution, crystallises from a mixture of chloroform and light petroleum in rosettes of needles, and melts and decomposes at 122°. G. Y.

Action of Hydroxylamine and a-Benzylhydroxylamine on Ethyl Hydroxytrimethylcomenate. E. Azzarello (*Atti R. Accad. Lincei*, 1905, [v], **14**, ii, 162—167).—Meyer (Abstr., 1884, 993) and Odernheimer (Abstr., 1884, 1302) have shown that comenic acid does not react with hydroxylamine, whilst ethylcomenic acid and ethyl diethylcomenate yield with it hydroxypyridine derivatives. Similarly, hydroxycomenic acid, being non-etherified, only gives a salt with hydroxylamine, or, when heated with excess of the latter, resinifies; the ester of its trimethyl derivative gives, however, a hydroxamic acid with hydroxylamine, but with a-benzylhydroxylamine reaction only takes place with difficulty, and yields probably the benzyl derivative of the corresponding oxypyridone compound.

Hydroxylamine hydroxycomenate separates from water in pale yellow crystals carbonising at about 200°, reduces Fehling's solution in the cold, and, when heated in alcoholic solution with piperonal, yields piperonaloxime.

2 : 3-*Dimethoxypyrone-6-carbonylhydroxamic acid*,

$$OH\cdot NH\cdot CO\cdot C{<}\begin{matrix}O\cdot C(OMe)\\CH\text{—}CO\end{matrix}{>}C\cdot OMe,$$

prepared by the interaction of ethyl hydroxytrimethylcomenate and hydroxylamine in alcoholic solution, crystallises from ethyl acetate in white needles, melting and decomposing at 178—179°, and is soluble in water, methyl or ethyl alcohol, or acetone. It has an acid reaction, reduces Fehling's solution and ammoniacal silver nitrate solution on heating, and gives a cherry-red coloration with ferric chloride and, with copper acetate, a green precipitate dissolving in excess of the acetate solution. Its *barium* salt, $(C_8H_8O_6N)_2Ba,2H_2O$, separates from water in small, white needles which undergo change at 110—120°. When heated with 20 per cent. sulphuric acid, the acid undergoes decomposition into hydroxylamine and dimethoxypyronecarboxylic acid.

T. H. P.

Basicity of Pyranic Oxygen. Double Salts of Halogen Derivatives of Dinaphthapyryl and of the Metals. Robert Fosse and L. Lesage (*Compt. rend.*, 1905, **141**, 625—626).—In addition to the double halogen salts of dinaphthapyryl and certain metals already described (compare this vol., i, 541), similar compounds containing the metals platinum, lead, iron, zinc, tin, bismuth, arsenic, or antimony have also been prepared; the formulæ of these new salts are given below, the dinaphthapyryl group $\left[\cdot CH{<}\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}{>}O\right]$ being represented by R: $PtBr_4,2RBr$, red powder. $PtCl_2,RCl$, violet-red crystals. $FeCl_3,RCl$, orange powder. $ZnCl_2,2RCl$, red crystals, yellow in reflected light. $3ZnBr_2,4RBr$, red crystals, green in reflected light. $SnBr_4,2RBr$, red crystals, yellow in reflected light. $BiBr_3,3RBr$, bright red powder. $AsBr_3,RBr$, red crystals. $SbBr_3,RBr$, red crystals.

M. A. W.

β-Coniceine. Karl Löffler (*Ber.*, 1905, **38**, 3326—3329. Compare Hofmann, Abstr., 1885, 401).—When conhydrine is heated with phosphoric oxide at 180—190° for 20 minutes, according to Wertheim (*Annalen*, 1856, **100**, 75) the products are β-coniceine and a small amount of a liquid, unsaturated, secondary base, but no α-coniceine. β-Coniceine has a sp. gr. 0·8519 at 50°/50° and $[\alpha]_D - 52\cdot99°$ at 42°. The *hydrochloride* crystallises in glistening needles and melts at 177—181°. The *aurichloride* melts at 122·5°, the *picrate* and *cadmioiodide* are oily.

Larger quantities of the oily base are obtained when the heating is carried out for a longer time and at a higher temperature, for example, for one hour at 220°.

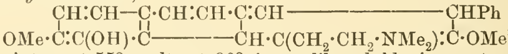
J. J. S.

Hydroxysparteine. Felix B. Ahrens (*Ber.*, 1905, **38**, 3268).—Hydroxysparteine, $C_{15}H_{24}ON_2$, is obtained in the theoretical yield by adding an alkaline solution of potassium ferricyanide to sparteine until the colour of the oxidising agent remains unchanged; the product is extracted with ether or chloroform.

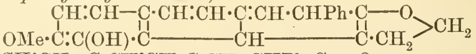
G. Y.

Action of Bromine on Strychnine. HEINRICH BECKURTS (*Arch. Pharm.*, 1905, **243**, 493—495. Compare Abstr., 1890, 1329).—When a dilute solution of strychnine hydrobromide is mixed with excess of bromine, *bromostrychnine tribromide*, $C_{21}H_{21}O_2N_2Br,Br_3$, is obtained as a yellow, crystalline powder, which carbonises without melting when heated, and is sparingly soluble in cold alcohol, insoluble in water. When heated at 105° or digested with cold alcohol, it is converted into a dibromide. Boiling with alcohol or treatment in the cold with alcoholic potassium hydroxide, hydrogen sulphide, or zinc and sulphuric acid converts it into bromostrychnine and a bromide or hydrobromic acid. C. F. B.

Thebaine. MARTIN FREUND (*Ber.*, 1905, **38**, 3234—3256).—Thebaine interacts with magnesium phenyl bromide in ethereal solution to form *phenyldihydrothebaine hydriodide*, $C_{25}H_{27}O_3N,HI$, which crystallises from water and melts at 230—232°, or from alcohol in prisms containing C_2H_6O and melting at 182—184°. The free *base* crystallises from a small quantity of alcohol in prisms and melts at 60—65°; the *sodium* derivative forms matted needles; the *hydrochloride*, $C_{25}H_{27}O_3N,HCl,C_2H_6O$, crystallises from alcohol in prisms and melts and decomposes at 145—147°; the *hydrobromide* crystallises in plates and melts and decomposes at 190—195°; the *methiodide*, $C_{26}H_{30}O_3NI$, crystallises from 50 per cent. alcohol in prisms and melts at 230—231°. When boiled with 30 per cent. potassium hydroxide or with sodium ethoxide solution, the methiodide yields *dephenyl*-N-*methyldihydrothebaine*,



which sinters at 55°, melts at 90°, is readily soluble in most organic solvents, and forms the *methiodide*, $C_{27}H_{32}O_3NI$. This crystallises from dilute alcohol in matted needles, sinters at 145—155°, and when boiled with concentrated aqueous potassium hydroxide or absolute alcoholic sodium ethoxide is decomposed with formation of trimethylamine and *phenyldihydrothebenol*,



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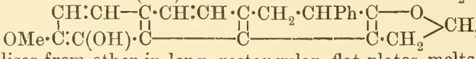
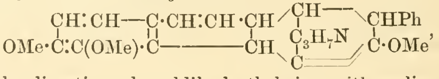


, which crystallises from ether in long, rectangular, flat plates, melts at 148—149°, forms a *sodium* derivative which is decomposed by water, and an *additive* compound with bromine in chloroform solution.

Phenyldihydrothebaine methyl ether,



is formed by digesting phenyldihydrothebaine with sodium ethoxide and methyl *p*-toluenesulphonate in alcoholic solution; it separates from aqueous alcohol as a flocculent precipitate which becomes crystalline, sinters at 60°, and is melted at about 70°. It combines with methyl

iodide to form the *methiodide*, $C_{27}H_{32}O_3NI$, which crystallises in long plates, melts at 209—210°, and when boiled with alcoholic sodium ethoxide yields *dephenyl*-N-*methyldihydrothebaine methyl ether*, which is obtained as a viscid, yellow oil; the *platinichloride*,

$$(C_{27}H_{31}O_3N)_2,H_2PtCl_6,$$

is amorphous and melts at 125—135°. When the base is treated with methyl iodide and the product boiled with sodium ethoxide solution, there is formed *a-phenyldihydrothebenol methyl ether*,

$$\left.\begin{array}{l} CH\!:\!CH\text{——}C\cdot CH\!:\!CH\cdot C\!:\!CH\cdot CHPh\cdot C\text{——}O \\ OMe\cdot C\!:\!C(OMe)\cdot C\text{————}CH\text{————}C\cdot CH_2 \end{array}\right> CH_2,$$

which is formed also by the action of methyl iodide and sodium ethoxide on phenyldihydrothebenol; it crystallises from alcohol in hexagonal prisms, melts at 114—115°, and is optically inactive. When heated over its melting point, the *a*-methyl ether changes into the *β-methyl* ether,

$$\left.\begin{array}{l} CH\!:\!CH\text{——}C\cdot CH\!:\!CH\cdot C\cdot CH_2\cdot CHPh\cdot C\text{——}O \\ OMe\cdot C\!:\!C(OMe)\cdot C\text{————}C\text{————}C\cdot CH_2 \end{array}\right> CH_2,$$

which is formed also when the *a*-isomeride is boiled with amyl alcohol or heated with acetic anhydride and sodium acetate in a sealed tube at 100°; it crystallises in rhombic plates, melts at 123—124°, and is optically inactive. Both ethers form unstable *additive* compounds with sodium ethoxide in alcoholic solution, and yield phenyldihydrothebenol when dried over soda-lime and treated with water.

Phenyldihydrothebaine ethyl ether methiodide, $C_{28}H_{34}O_3NI$, is formed when phenyldihydrothebaine is treated with sodium ethoxide and ethyl iodide in alcoholic solution on the water-bath and the oily product boiled with methyl iodide and a small quantity of alcohol in a reflux apparatus; it crystallises from dilute alcohol in long prisms, melts at 209—210°, and when boiled with concentrated sodium ethoxide solution yields *dephenyl*-N-*methyldihydrothebaine ethyl ether*, which is a viscid oil with blue fluorescence, is soluble in acids, and on digestion with methyl iodide and a small quantity of alcohol yields the *methiodide*, $C_{29}H_{36}O_3NI$. This crystallises in white plates, melts at 247—248°, and when digested with sodium ethoxide solution yields an amine and *phenyldihydrothebenol ethyl ether*,

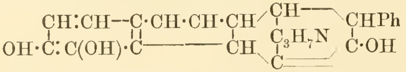
$$\left.\begin{array}{l} CH\!:\!CH\text{—}C\cdot CH\!:\!CH\cdot C\!:\!CH\cdot CHPh\cdot C\text{——}O \\ OMe\cdot C\!:\!C(OEt)\cdot C\text{————}CH\text{————}C\cdot CH_2 \end{array}\right> CH_2,$$

which is formed also by the action of sodium ethoxide and ethyl iodide on phenyldihydrothebenol, crystallises in long, flat prisms, and melts at 97—98°. When boiled with acetic anhydride and sodium acetate, phenyldihydrothebaine forms an *acetyl* derivative, $C_{27}H_{29}O_4N$, which forms a granular mass, sinters at 65—70°, melts at 92°, and forms a *methiodide*, $C_{28}H_{32}O_4NI$; this crystallises in short, stout prisms and melts at 202—203°.

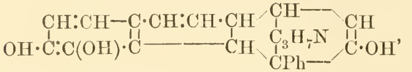
When boiled with hydriodic acid of sp. gr. 1·7, phenyldihydrothebaine hydriodide yields methyl iodide and the *hydriodide* of *nor*-phenyldihydrothebaine, which crystallises from water in matted needles and melts at about 185—190°; the *hydrochloride*,

$$C_{23}H_{23}O_3N,HCl,$$

formed by the action of hydrochloric acid of sp. gr. 1·19 in a sealed tube at 100°, crystallises in matted, white needles, sinters at 190—200°, and decomposes at 200—220°. The free *base*,

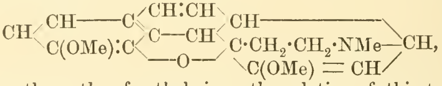


or



crystallises from hot water in matted needles, sinters at 120—125°, forms crystalline *salts* with sulphuric and acetic acids, and dissolves in aqueous sodium hydroxide, yielding an odour of benzaldehyde. When digested with sodium ethoxide and methyl iodide in alcoholic solution, dihydrothebaine methiodide (Freund and Holthof, Abstr., 1899, i, 307) forms the *methiodide* of dihydrothebaine methyl ether, $C_{21}H_{28}O_3NI$, which crystallises in leaflets, melts at 192°, is insoluble in aqueous alkali hydroxides, and when boiled with 30 per cent. aqueous potassium hydroxide yields *de-N-methyldihydrothebaine*; this is converted by digestion with methyl iodide in ethereal solution into the crystalline *methiodide*, which, when boiled with 30 per cent. aqueous potassium hydroxide, yields methylthebaol; this is identified by conversion into its picrate, melting at 110—112° (Pschorr, Seydel, and Stöhrer, Abstr., 1903, i, 167; Vongerichten, *ibid.*, i, 168).

The formulæ given for the substances described in this paper are derived from the formula



suggested by the author for thebaine; the relation of this to the constitutions of codeine and methylmorphimethine and their derivatives is discussed. G. Y.

Thebainone: a Ketone obtained by Reduction of Thebaine. Robert Pschorr (*Ber.*, 1905, **38**, 3160—3170).—*Thebainone*, $C_{18}H_{21}O_3N$, is formed by heating thebaine with stannous chloride and hydrochloric acid in a sealed tube at 100°; it crystallises from methyl alcohol (with CH_4O) in yellow prisms melting at 115—118° (corr.), or from water in colourless scales melting at 89—90° (corr.). It is easily soluble in acetone, alcohol, chloroform, ethyl acetate, or benzene, less so in methyl alcohol, and only sparingly so in ether or hot water; the aqueous solution is yellow, has a slight alkaline reaction, becomes almost colourless when slightly acidified, and on evaporation yields a yellow, resinous mass which is easily soluble in water. The *sodium* derivative, $C_{18}H_{20}O_3NNa$, crystallises in glistening, yellowish-red plates and forms a red, aqueous solution; the *picrate*,

$$C_{18}H_{21}O_3N,C_6H_3O_7N_3,$$

crystallises in yellow prisms, melts at 250—253° (corr.), and is easily decomposed by ammonia. The *oxime*, $C_{18}H_{22}O_3N_2$, crystallises from a mixture of ethyl acetate and light petroleum in colourless prisms melt-

ing at 200—201° (corr.), or from methyl alcohol in yellow needles containing CH_4O; the *semicarbazone*, $C_{19}H_{24}O_3N_4$, crystallises in colourless needles and melts at 227° (corr.); the *phenylhydrazone* is not crystalline; the *methiodide*, $C_{19}H_{24}O_3NI$, crystallises in colourless prisms and melts at 255—256° (corr.). The *acetyl* derivative, $C_{20}H_{23}O_4N$, crystallises in small prisms and melts at 100—101° (corr.); the *methiodide* of the acetyl derivative, $C_{21}H_{26}O_4NI$, crystallises from the concentrated alcoholic solution in colourless prisms and melts at 223—225° (corr.); the *semicarbazone* of acetylthebainone crystallises from ethyl acetate in colourless needles and melts at 249° (corr.); the *phenylhydrazone*, $C_{26}H_{29}O_3N_3$, forms yellow prisms and melts at 225—226° (corr.).

Thebainol, $C_{18}H_{23}O_3N$, is obtained when the ketone is reduced with sodium amalgam in dilute sodium hydroxide solution; it crystallises from its concentrated methyl-alcoholic solution in colourless, prismatic needles, and melts at 54—55° or, after fusion in a vacuum and resolidification, at 76—78° (corr.).

Thebainone methyl ether (methylthebainone), $C_{19}H_{23}O_3N$, can be prepared by treating the ketone with diazomethane in ethereal alcoholic solution; it crystallises from methyl alcohol in slightly yellow, prismatic plates and melts at 156° (corr.). The action of methyl iodide on the ketone or its methyl ether in sodium methoxide solution leads to the formation of *methylthebainone methiodide*, $C_{20}H_{26}O_3NI$, which crystallises in hexagonal leaflets and melts at 256° (corr.). When warmed with 30 per cent. aqueous sodium hydroxide, this yields *methylthebainonemethine*, $C_{20}H_{25}O_3N$, which crystallises from a mixture of ether and light petroleum in slender, yellow needles, and, after being dried at 90° in a vacuum, melts at 65—66° (corr.). The *methiodide*, $C_{21}H_{28}O_3NI,C_2H_6O$, crystallises from its ethereal-alcoholic solution in glistening, yellow needles, loses C_2H_6O at 100°, and melts at 171—172° (corr.). The *semicarbazone* of methylthebainonemethine,

$$C_{21}H_{28}O_3N_4,C_2H_6O,$$

crystallises in long, yellow, hexagonal leaflets, sinters at 85°, and melts at 107—108° (corr.), or, after losing C_2H_6O at 90° in a vacuum, at 126—127° (corr.). The *hydrochloride* of methylthebainonmethine oxime, $C_{20}H_{26}O_3N_2,HCl$, formed by the action of hydroxylamine hydrochloride and sodium acetate on the ketone in acetic acid solution, crystallises in yellow prisms, melts at 271—272° (corr.), and on treatment with aqueous potassium carbonate yields an amorphous *base* which is easily soluble in the usual organic solvents.

To explain the formation of a ketone on reduction of thebaine, the author suggests the formulæ

```
                 CH:CH·C·CH₂·CH———NMe·CH₂
                 |     ||    |           |
      OMe·C═C—C—C═C———————CH·CH₂
             |       |              |
             O———CH·C(OMe):CH
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Thebaine.

and

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         CH:CH—C·CH₂—CH—NMe·CH₂
         |     ||     |       |
OMe·C:C(OH)·C—C═C——————CH·CH₂
               |       |
              CH₂—CO—CH₂
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Thebainone.

G. Y.

Thebainone from Codeinone. LUDWIG KNORR (*Ber.*, 1905, 38, 3171. Compare preceding abstract).—Thebainone is formed by reduction of codeinone with stannous chloride and hydrochloric acid in a sealed tube at 100°; it is a dihydrocodeinone isomeric with codeine.

G. Y.

Decomposition Products of Thebainone. LUDWIG KNORR and ROBERT PSCHORR (*Ber.*, 1905, 38, 3172—3181. Compare preceding abstracts).—Thebainone, $OMe\cdot C_{14}H_{10}O(OH){<}{\begin{smallmatrix}C_2H_4\\ |\\ NMe\end{smallmatrix}}$, stands between codeinone, $OMe\cdot C_{14}H_9O_2{<}{\begin{smallmatrix}C_2H_4\\ |\\ NMe\end{smallmatrix}}$, on the one hand, and morphothebaine, $OMe\cdot C_{14}H_7(OH)_2{<}{\begin{smallmatrix}C_2H_4\\ |\\ NMe\end{smallmatrix}}$, and thebinine,

$$OMe\cdot C_{14}H_6(OH)_2\cdot C_2H_4\cdot NHMe,$$

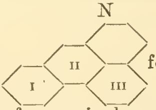
on the other. It resembles the last two in the presence of a hydroxyl group in the place of the indifferent oxygen atom of the opium alkaloids, but differs from them in its degree of reduction.

A table is given showing the most important decomposition products of the opium alkaloids and their derivatives, and the following conclusions are drawn as to the constitutions of morphine, codeine, and thebaine: (1) they are derivatives of 3 : 6-dihydroxyphenanthrylene oxide,

$$\begin{array}{l} \qquad\quad\;\ulcorner\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\, O \,-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!\urcorner \\ OH\cdot C{=\!=}C\cdot C{-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-}C\cdot C{=}C\cdot OH \\ \quad\;\, CH{:}CH\cdot C\cdot CH{:}CH\cdot C\cdot CH{:}CH \end{array}$$

; in codeine one, and in thebaine two of the hydroxyl groups are methylated. (2) The group $\cdot C_2H_4\cdot NMe\cdot$ is attached to the phenanthrene nucleus as a side ring; it remains to be determined whether as the group $\cdot CH_2\cdot CH_2\cdot NMe\cdot$ or as $\cdot CHMe\cdot NMe\cdot$, but the constitution of papaverine,

$$\begin{array}{l} OMe\cdot C{:}CH\cdot C\cdot C[CH_2\cdot C_6H_3(OMe)_2]{:}N \\ OMe\cdot C{:}CH\cdot C\cdot CH{=\!=\!=\!=\!=\!=}CH, \end{array}$$

points to the structure  for the nucleus of the morphine alkaloids. (3) So far as is known at present, morphine is 3 : 6-dihydroxy-8 : 9(?)-ethylenemethylaminohexahydrophenanthrylene 4 : 5-oxide, the rings II and III of the phenanthrene nucleus being reduced, whilst I remains as a benzene ring; codeine is 6-hydroxy-3-methoxy-8 : 9(?)-ethylenemethylaminohexahydrophenanthrylene 4 : 5-oxide; and thebaine, 3 : 6-dimethoxy-8 : 9(?)-ethylenemethylaminophenanthrylene 4 : 5-oxide.

When heated with acetic anhydride at 170—180° for 48 hours, methylthebainonemethine yields dimethylmorphol melting at 43—44°, and dimethylhydroxyethylamine. This shows that the formation of alcohol bases is not dependent on a linking of the group $\cdot C_2H_4\cdot NMe\cdot$, by means of an oxygen atom, to the phenanthrene nucleus, but may take place by solution of a carbon union.

Methylthebainonemethine is decomposed by sodium ethoxide in

alcoholic solution at 150—160° with formation of a resinous phenanthrene derivative and dimethylethylamine, which forms an aurichloride melting at 220° and a *platinichloride* decomposing at about 240° (compare Skraup and Wiegmann, Abstr., 1889, 1018).

The *base* obtained on treating methylthebainonemethine methiodide with silver oxide decomposes at 150—160°, with formation of a phenanthrene derivative and trimethylamine. G. Y.

Complex Molybdenum Thiocyanates. JULIUS SAND and O. BURGER (*Ber.*, 1905, **38**, 3384—3389).—When a solution of ammonium molybdate and ammonium thiocyanate is reduced electrolytically and the resulting liquid extracted with ether, all the red colouring substances pass into the latter; on adding pyridine, *molybdenumdipyridinetetrathiocyanate*, $Mo[(C_5H_5N)_2(SCN)_4]$, is obtained in the form of dark brownish-red, feathery aggregates of crystals. When the foregoing red solution is extracted with amyl alcohol and a large excess of pyridine is added, the *hexathiocyanate*,

$$Mo(C_5H_5N,HCNS)_2(C_5H_5N)_4(CNS)_4,$$

is obtained; it crystallises in well-formed, bright yellow plates and melts at 115°.

Molybdenumtetraquinolinetetrathiocyanate, $Mo(C_9H_7N)_4(CNS)_4$, obtained by adding quinoline to the ethereal extract of the foregoing reduced solution, forms beautiful, brownish-violet crystals.

Molybdenumhexapyridinedecachloride, $Mo(C_5H_5N,HCl)_6Cl_4$, is obtained by passing hydrogen chloride into a solution of molybdenumdipyridinetetrathiocyanate in acetone; it forms yellowish-green, hygroscopic crystals. The probable relationship of the foregoing substances is discussed. W. A. D.

Dinitrophenylpyridinium Chloride and its Transformation Products. IV. The Action of Aliphatic Amines on Dinitrophenylpyridinium Chloride. THEODOR ZINCKE and W. WÜRKER (*Annalen*, 1905, **341**, 365—379. Compare Abstr., 1904, i, 921).—The aliphatic amines differ from the aromatic amines in their behaviour towards dinitrophenylpyridinium chloride. Amorphous substances which yield red hydrochlorides are at first formed, dinitroaniline not being eliminated. Prolonged treatment, however, causes the formation of dinitroaniline and quaternary pyridinium salts. The red salts are related to the substances produced by the action of alkalis and phenylhydrazine on the pyridinium compound. These red salts are represented by the formula $[C_6H_3(NO_2)_2{\cdot}C_5NH_5]{\cdot}NHAlk,HCl$; they are decomposed by aniline with the formation of the dianilide (compare Abstr., 1904, i, 923). When heated with hydrochloric acid, dinitroaniline is formed, and a pyridinium salt, C_5NH_5AlkCl, in the case of the compounds of primary amines. The products obtained from secondary amines are decomposed to a much greater extent by hydrochloric acid. Primary aliphatic amines do not yield compounds corresponding with the dianilides. Secondary amines, on the other hand, give such compounds, which, however, are unstable.

The *methylamine* compound,

$$C_6H_3(NO_2)_2{\cdot}N{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}NH_2MeCl,$$

prepared by addition of 10 per cent. aqueous methylamine to a solution of dinitrophenylpyridinium chloride, followed by addition of hydrochloric acid, crystallises in intensely red leaflets, melting and decomposing at 120—121°. The *platinichloride* is a pale red, crystalline powder, melting and decomposing at 150°. The free base is a dark brown precipitate. The *ethylamine* compound, $C_{13}H_{15}O_4N_4Cl$, forms red, metallic needles melting and decomposing at 105°; the *ethylenediamine* compound melts and decomposes at 131—133°. Methylpyridinium chloride, C_5NH_5MeCl, prepared by heating the methylamine derivative with hydrochloric acid, or directly from dinitrophenylpyridinium chloride, forms a *mercurichloride*, which crystallises in needles melting and decomposing at 189—191°. The *platinichloride*, $(C_5NH_5Me)_2PtCl_6$, crystallises in orange-yellow leaflets melting at 203—204°.

The *dimethylamine* compound,

$$C_6H_3(NO_2)_2\cdot N{:}CH\cdot CH{:}CH\cdot CH{:}CH\cdot NHMe_2Cl,$$

prepared in the same manner as the methylamine compound, crystallises in pale yellow needles melting and decomposing at 116—117°; the *platinichloride* is a brick-red, crystalline powder. The *diethylamine* compound crystallises in red needles melting and decomposing at 170°. The *piperidine* compound,

$$C_6H_3(NO_2)_2\cdot N{:}CH\cdot CH{:}CH\cdot CH{:}CH\cdot C_5NH_{11}Cl,$$

crystallises in red needles melting and decomposing at 126—128°; the *platinichloride* is a dark red, crystalline powder melting and decomposing at 179—180°. With excess of dimethylamine, the dinitrophenylpyridinium chloride yields a *compound*,

$$NMe_2\cdot CH{:}CH\cdot CH{:}CH\cdot CH{:}NMe_2Cl,$$

the *platinichloride* of which crystallises in orange-red plates melting and decomposing at 153—154°. The *mercurichloride* is a pale yellow precipitate and the *stannochloride* a pale brown precipitate, while the *double salt* with cadmium sulphate crystallises in yellow needles. Excess of piperidine produces a *compound*,

$$C_5NH_{10}\cdot CH{:}CH\cdot CH{:}CH\cdot CH{:}C_5NH_{10}Cl,$$

which forms a *mercurichloride*, $C_{15}H_{25}N_2Cl,HgCl_2$, as a yellow, crystalline, unstable precipitate melting and decomposing at 183°.

K. J. P. O.

A New Methyleneindoline Base. ARTUR KONSCHEGG (*Monatsh.*, 1905, **26**, 931—937. Compare Brunner, Abstr., 1896, i, 169, 253; 1900, i, 360).—The p-*tolylhydrazone* of methyl *iso*propyl ketone forms a slightly yellow oil, which boils at 164° under 30 mm. pressure and rapidly becomes red on exposure to air. When treated with an alcoholic solution of stannous chloride and hydrochloric acid after eight days at the ordinary temperature, warmed on the water-bath, and finally precipitated with ether and hydrogen chloride, the hydrazone yields the *stannochloride* of 3 : 3 : 5-trimethyl-2-methyleneindoline. The *base*,

$$C_6H_3Me{<}{}^{CMe_2}_{NH-}{>}C{:}CH_2,$$

forms a red, aromatic oil, which boils at 170° under 30 mm. pressure and is readily soluble in alcohol, ether, or acids. The *picrate*,

$$C_{18}H_{18}O_7N_4,$$

crystallises in slender, yellow needles and melts at 195°; the *mercurichloride* crystallises in long needles; the *platinichloride*,

$$(C_{12}H_{15}N)_2,H_2PtCl_6,$$

forms a bronze-red powder; the *ferrichloride* is obtained as an oil. With potassium nitrite and dilute sulphuric acid, the base forms an oily *nitrosoamine*, which gives Liebermann's reaction. The *acetyl* derivative crystallises from light petroleum and is hydrolysed by boiling 20 per cent. aqueous sodium hydroxide; the aqueous solution yields a residue which gives the cacodyl reaction. The *benzoyl* derivative crystallises from dilute alcohol in thread-like needles.

Plancher's supposed 2 : 3 : 3-trimethylindolenine (Abstr., 1898, i, 536) is 3 : 3-dimethyl-2-methyleneindoline. G. Y.

Action of Bromine on Chloroindole and of Sulphuryl Chloride on Scatole. Girolamo Mazzara and Alessandro Borgo (*Gazzetta*, 1905, **35**, ii, 326—333. Compare following abstract).—The constitution of the compound formed by the action of sulphuryl chloride (1 mol.) on indole (1 mol.) is proved by treating it with bromine (1 mol.), which converts it into *2-chloro-3-bromo-indole*, C_8NH_5ClBr; this compound crystallises from light petroleum in faintly yellow, shining scales turning brown at 85° and softening and decomposing at 92°; it dissolves in dilute potassium hydroxide solution and in concentrated sulphuric acid, to which it imparts an intensely green colour. When heated, in methyl-alcoholic solution, with alcoholic potassium hydroxide and methyl iodide, it yields *2-chloro-3-bromo-1-methylindole*, $C_8NH_4MeClBr$, which crystallises from aqueous alcohol in slender, silky needles melting at 59°, and dissolves in the cold in concentrated sulphuric acid, giving it a yellow, and later a green coloration.

2-Chloro-3-methylindole, C_8NH_5MeCl, prepared by the action of sulphuryl chloride (1 mol.) on scatole (1 mol.), crystallises from light petroleum in small, white leaflets readily turning yellow, even in presence of the solution, and melts at 112°; it has an intense, rather pleasing odour and is soluble to a slight extent in water and more readily in concentrated sulphuric acid, to which it imparts a pale yellow coloration. T. H. P.

Action of Sulphuryl Chloride on Indole. Girolamo Mazzara and Alessandro Borgo (*Gazzetta*, 1905, **35**, ii, 320—326. Compare this vol., i, 827).—Sulphuryl chloride acts on indole with apparent formation of monochloroindole, which could not be purified, as it readily changes into oxindole. The latter separates from light petroleum in long needles or prisms melting at 125°, which is some 5° higher than the melting points given by Baeyer and Knop (*Annalen*, 1866, **140**, 29) and by König and Reissert (Abstr., 1899, i, 457). Oxindole can only be formed by the action of water on 2-chloroindole, but all attempts to separate the latter from the other products of the action of sulphuryl chloride on indole have been unsuccessful. T. H. P.

Introduction of Benzoyl Groups into Tertiary Cyclic Bases. II. Arnold Reissert (*Ber.*, 1905, **38**, 3415—3435. Compare this vol., i, 472).—The substance formed by the action of benzoyl chloride

and sodium hydroxide on quinoline, and supposed to be 2-hydroxy-1-benzoyl-1 : 2-dihydroquinoline (*loc. cit.*), is really o-*benzoylaminocinnamaldehyde*, $NHBz\cdot C_6H_4\cdot CH:CH\cdot CHO$. With hydroxylamine, it gives the *oxime*, $NHBz\cdot C_6H_4\cdot CH:CH\cdot CH:N\cdot OH$, which crystallises from methyl or ethyl alcohol in small needles and melts and decomposes at 170—171°. The *phenylhydrazone*,

$$NHBz\cdot C_6H_4\cdot CH:CH\cdot CH:N_2HPh,$$

crystallises from glacial acetic acid in small, yellow needles and melts at 183—184°.

o-*Benzoylaminocinnamylideneaniline*,

$$NHBz\cdot C_6H_4\cdot CH:CH\cdot CH:NPh,$$

prepared by the action of aniline on the aldehyde, crystallises from alcohol in pale yellow needles and melts at 144—145°; on prolonged boiling with alcohol, it is decomposed, giving benzanilide and quinoline. *o*-Benzoylaminocinnamaldehyde does not interact with methylaniline.

o-*Benzoylaminocinnamic acid*, $NHBz\cdot C_6H_4\cdot CH:CH\cdot CO_2H$, prepared by oxidising the aldehyde with silver oxide in presence of sodium hydroxide in alcohol, crystallises from alcohol in small, flat needles and melts and decomposes at 262°; it is identical with the substance prepared by benzoylating *o*-aminocinnamic acid, and on hydrolysis with hydrochloric acid at 160—180° gives benzoic acid and carbostyril. The substance formerly described as *o*-benzoylaminocinnamic acid (Walter, Abstr., 1892, 881) and prepared by the oxidation of *N*-benzoyltetrahydroquinaldine, has apparently another structure (perhaps 1-benzoylhydroindole-2-carboxylic acid,

$$C_6H_4<\begin{matrix}CH_2\\NBz\end{matrix}>CH\cdot CO_2H),$$

as on hydrolysis it gives benzoic acid, carbon dioxide, indole, and hydrogen.

o-*Benzoylamino-β-phenylpropionic acid*, $NHBz\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CO_2H$, prepared by reducing *o*-benzoylaminocinnamic acid with sodium amalgam and benzoylating the product (o-*amino-β-phenylpropionic acid*) in alkaline solution, forms small, soft crystals and melts indefinitely at 153—170°.

On warming *o*-benzoylaminocinnamaldehyde with alcoholic potassium hydroxide, an *acid* is formed according to the equation $2C_{16}H_{13}O_2N + H_2O = C_{32}H_{28}O_5N_2$; on precipitating with hydrochloric acid, the *lactone*, $C_{32}H_{26}O_4N_2$, is obtained, which crystallises from acetone in small, hard, very white crystals and melts at 268—269°. The *sodium* salt,

$$C_{32}H_{27}O_5N_2Na,$$

and *silver* salt, $C_{32}H_{27}O_5N_2Ag$, of the acid were prepared. On heating the lactone with concentrated hydrochloric acid at 160—170°, a *base*, $C_{18}H_{16}ON_2$, is formed which gives, on benzoylation, a *benzoyl* derivative, $C_{25}H_{20}O_2N_2$; this crystallises from acetic acid in small prisms, sinters at 158°, and decomposes at 174°. The probable nature of the foregoing substances is discussed.

When *iso*quinoline is caused to interact with benzoyl chloride and potassium cyanide at the ordinary temperature, 1-*cyano*-2-*benzoyl*-1 : 2-*dihydro*iso*quinoline*, $C_6H_4<\begin{matrix}CH{=\!=}CH\\C(NBz)\cdot CH\cdot CN,\end{matrix}$ is formed; it crystallises from alcohol in small, colourless prisms, melts at 125—126°, and is

decomposed by concentrated hydrochloric acid at the ordinary temperature, giving a mixture of iso*quinaldic acid* (iso*quinoline*-1-*carboxylic acid*) and its *amide*. The former separates from benzene in compact, yellow crystals, melts and decomposes at 161°; the latter crystallises from benzene in small needles and melts at 168—169°. Two other *substances*, the one melting at 151°, the other, $C_{34}H_{23}ON_3$, at 123—124°, are produced in small quantity at the same time.

When benzthiazole in aqueous suspension is acted on by benzoyl chloride and sodium hydroxide, a mixture of 1-phenylbenzthiazole and *dibenzoyl*-o-*aminothiophenol*, $NHBz\cdot C_6H_4\cdot SBz$, is obtained; the latter crystallises from alcohol in thin needles, melts at 154—155°, and when boiled with 10 per cent. sodium hydroxide gives *oo'*-diaminodiphenyl disulphide. It is probable that the foregoing products are formed in accord with the equations: I. $C_6H_4{<}{\overset{S}{\underset{N}{}}}{>}CH + Ph\cdot CO\cdot OH =$

$$CHO\cdot S\cdot C_6H_4\cdot N{:}CPh\cdot OH = CHO\cdot S\cdot C_6H_4\cdot NH\cdot COPh.$$

II. $CHO\cdot S\cdot C_6H_4\cdot NH\cdot COPh + H_2O = SH\cdot C_6H_4\cdot NH\cdot COPh + H\cdot CO_2H.$

III. $SH\cdot C_6H_4\cdot N{:}CPh\cdot OH = H_2O + C_6H_4{<}{\overset{S}{\underset{N}{}}}{>}CPh.$

Pyridine and acridine could not be made to interact with benzoyl chloride in presence of either sodium hydroxide or potassium cyanide.

W. A. D.

Dihydroxyacridone and its Derivatives. W. Baczyński and Stefan von Niementowski (*Ber.*, 1905, **38**, 3009—3017. Compare Niementowski, Abstr., 1896, i, 261).—2 : 4-Dihydroxyacridone and its anilide are formed along with hydroxyquinacridone when anthranilic acid and phloroglucinol are heated together at 170—190° for half an hour. On extraction of the product with boiling acetone, 2 : 4-dihydroxyacridone and its anilide dissolve, the former crystallising out first on concentration of the solution.

2 : 4-*Dihydroxyacridone*, $C_6H_4{<}\begin{matrix}NH\cdot C{-}CH{=}C\cdot OH \\ CO{-}C\cdot C(OH){:}CH\end{matrix}$, may be obtained from the reaction product also by extraction with boiling aqueous sodium hydroxide, and is then purified by means of its sodium derivative; it crystallises in canary-yellow, nodular aggregates of needles, melts at 370°, is easily soluble in acetone, less so in methyl or ethyl alcohol, ethyl acetate, or glacial acetic acid, and only sparingly so in boiling water, has marked acid properties, and is easily soluble in aqueous ammonia or alkali hydroxides, but insoluble in dilute acids. The *sodium* derivative, $C_{13}H_8O_3NNa,5H_2O$, crystallises in slender, glistening, yellow needles, dyes silk yellow, and is decomposed by carbon dioxide in aqueous solution. The *acetyl* derivative, $C_{13}H_8O_3NAc$, formed by boiling 2 : 4-dihydroxyacridone with acetic anhydride and sodium acetate, separates from ethyl acetate in stout yellow crystals, softens at 195°, melts at 200°, is more soluble than the dihydroxyacridone in organic solvents, dissolves readily in aqueous alkali hydroxides, sparingly in ammonia, and is insoluble in dilute acids; it is very stable towards hydrolysing agents. The *benzoyl* derivative, $C_{20}H_{13}O_4N$, formed by the Schotten-Baumann method, crystallises in glistening, greenish-yellow, thin leaflets and melts at

295—297°. The action of methyl iodide on the sodium derivative of 2 : 4-dihydroxyacridone in methyl-alcoholic solution at 150° leads to the formation of two monomethyl ethers. The *a-methyl ether*, $C_{14}H_{11}O_3N$, crystallises in spherical, chocolate-coloured aggregates, sinters at 190°, melts at 203°, and is moderately soluble in hot alcohol, acetone, aqueous ammonia, or alkali hydroxides. The *β-methyl ether* crystallises in glistening, yellow, thin leaflets, sinters at 235°, melts and decomposes at 252°, and is more soluble than the a-isomeride in organic solvents.

The action of a large excess of methyl sulphate on 2 : 4-dihydroxyacridone leads to the formation of the β-monomethyl ether and 2 : 4-*dimethoxyacridone*, $C_{15}H_{13}O_3N$, which crystallises in green, nodular aggregates, becomes a dull green at 225°, and melts and decomposes at 286—287°; it is in general less soluble than the β-, but more so than the a-monomethyl ether.

*a-Nitro-*2 : 4-*dihydroxyacridone*, $C_{13}H_8O_5N_2$, is formed by the action of boiling dilute nitric acid on 2 : 4-dihydroxyacridone; it separates from organic solvents in yellow crystals, melts and decomposes at 257°, and is soluble in aqueous alkali hydroxides, ammonia, or mineral acids.

*β-Nitro-*2 : 4-*dihydroxyacridone*, formed by the action of nitric acid of sp. gr. 1·55 at 0—3° on 2 : 4-dihydroxyacridone, separates from acetone in dark brown crystals, becomes green at 180°, melts and decomposes at 268°, and is soluble in aqueous alkali hydroxides or ammonia, but only sparingly so in dilute acids.

The *anilide*, $C_{19}H_{14}O_2N_2$, crystallises in metallic, yellow, microscopic leaflets, melts at 269—270°, is easily soluble in methyl or ethyl alcohol, acetic acid or acetone, and yields aniline and 2 : 4-dihydroxyacridone when heated with concentrated hydrochloric acid at 200°.

An isomeric *anilide*, melting at 138—140°, is formed when dihydroxyacridone is heated with aniline in a sealed tube at 200°. G. Y.

a′-Methyl-a-pyrophthalone. ALEXANDER EIBNER (*Ber.*, 1905, **38**, 3353—3354. Compare Scholze, this vol., i, 825).—Scholze's 2-methyl-6-pyrophthalone is represented as having the constitution

$$C_6H_4{<}{}^{CO}_{CO}{>}CH\cdot C_5NH_2Me,$$

and as it is a *pseudo*-acid, its sodium salt is

$$C_6H_4{<}{}^{\quad CO\quad}_{C(ONa)}{>}C\cdot C_5H_3NMe.$$

J. J. S.

Derivatives of Diacetonalkamines. IV. MORITZ KOHN (*Monatsh.*, 1905, **26**, 939—949. Compare Abstr., 1904, i, 378, 932, 933).—2-Oxy-4 : 4 : 6-trimethyltetrahydro-1 : 3-oxazine,

$$O{<}{}^{CO\text{——}NH}_{CHMe\cdot CH_2}{>}CMe_2,$$

is formed by the action of ethyl chlorocarbonate on diacetonalkamine in ethereal solution, or by treating the hydrobromide of δ-bromo-β-amino-β-methylpentane (Kahan, Abstr., 1897, i, 494) with silver carbonate in boiling aqueous solution; it crystallises from a mixture

of benzene and light petroleum in white leaflets, melts at 128—131°, and boils at about 301°.

2-Oxy-3 : 4 : 4 : 6-tetramethyltetrahydro-1 : 3-oxazine,

$$O<\begin{matrix}CO\text{———}NMe\\CHMe\cdot CH_2\end{matrix}>CMe_2,$$

formed by the action of ethyl chlorocarbonate on methyldiacetonalkamine, crystallises from a mixture of benzene and light petroleum, melts at 84—87°, and boils at about 286°.

The action of ethylene oxide on diacetonalkamine in aqueous solution at 0°, leads to the formation of ethanoldiacetonalkamine and an extremely viscid liquid of high boiling point which may be *diethanoldiacetonalkamine.*

Ethanoldiacetonalkamine, $OH\cdot CHMe\cdot CH_2\cdot CMe_2\cdot NH\cdot CH_2\cdot CH_2\cdot OH$, forms a colourless, almost odourless, viscid liquid, boils at 154—155° under 13—14 mm. pressure, and is soluble in water; the *platinichloride,* $(C_8H_{19}O_2N)_2,H_2PtCl_6$, is obtained as a sandy, crystalline powder or in glistening needles.

The action of ethylene oxide on methyldiacetonalkamine in aqueous solution at 0° leads to the formation of *ethanolmethyldiacetonalkamine,* $OH\cdot CHMe\cdot CH_2\cdot CMe_2\cdot NMe\cdot CH_2\cdot CH_2\cdot OH$, which is obtained as a colourless, odourless, viscid liquid boiling at 146° under 11 mm. pressure; the *platinichloride,* $(C_9H_{21}O_2N)_2,H_2PtCl_6$, forms an ochre-coloured precipitate.

Methyldiacetonalkamine aurichloride, $C_7H_{17}ON,HAuCl_4$, melting at 101—103°, and *dimethyldiacetonalkamine aurichloride,*

$$C_8H_{19}ON,HAuCl_4,$$

melting at 185°, are described. G. Y.

Hydroxy-β-*iso*hexylamine. Moritz Kohn (*Monatsh.*, 1905, **26**, 951—958. Compare Kohn and Lindauer, Abstr., 1903, i, 73).—Hydroxy-β-*iso*hexylamine is oxidised by chromic acid in boiling sulphuric acid solution with formation of acetone, alanine, and acetic acid.

Hydroxy-β-*iso*hexylamine and propaldehyde condense at the laboratory temperature to form 4 : 6 : 6-*trimethyl*-2-*propyltetrahydro*-1 : 3-*oxazine,* $O<\begin{matrix}CHPr^{a}\cdot NH\\CMe_2\text{—}CH_2\end{matrix}>CHMe$, which is obtained as a colourless, mobile liquid possessing a characteristic ammoniacal odour of spice; it boils at 165—168° under 750 mm. pressure. The *platinichloride,* $(C_9H_{19}ON)_2,H_2PtCl_6$, forms sheaves of spicular crystals. The *nitroso*-derivative, $C_9H_{18}O_2N_2$, is obtained as a yellow oil having an odour of musk. With benzaldehyde at 120°, hydroxy-β-*iso*hexylamine condenses to form 2-*phenyl*-4 : 6 : 6-*trimethyltetrahydro*-1 : 3-*oxazine,* $O<\begin{matrix}CHPh\cdot NH\\CMe_2\cdot CH_2\end{matrix}>CHMe$, which is a colourless oil, boiling at 145—146° under 13 mm. pressure. The *platinichloride,* $(C_{13}H_{19}ON)_2,H_2PtCl_6$, forms nodular crystals; the *nitroso*-derivative is obtained as a viscid oil. When heated with dilute hydrochloric acid in a sealed tube in the water-bath, the oxazine formed from benzaldehyde and hydroxy-β-*iso*hexylamine is hydrolysed with formation of its generators.

G. Y.

Phenyl*iso*oxazolone. ALFRED TINGLE (*Amer. Chem. J.*, 1905, **34**, 471—472).—Phenyl*iso*oxazolone, recently described by Posner (Abstr., 1905, i, 577) was first prepared by Claisen and Zedel (Abstr., 1891, 468) and subsequently by the author (Abstr., 1900, i, 544). E. G.

Azoxonium Compounds. II. FRIEDRICH KEHRMANN (*Ber.*, 1905, **38**, 2952—2962. Compare Abstr., 1901, i, 484; this vol., i, 949).—The action of *o*-aminophenol on phenanthraquinone in boiling benzene or alcoholic solution leads to the formation of the *ψ-base*, $\begin{array}{l} C_6H_4\cdot C\cdot N(OH) \\ C_6H_4\cdot C \text{———} O \end{array} > C_6H_4$, which crystallises in silvery, almost colourless leaflets, melts at 206°, is soluble in glacial acetic acid, forms, in concentrated sulphuric acid, a bluish-violet solution which, on dilution, becomes red and finally yellow, and forms the unstable yellow *ψ-base*, $\begin{array}{l} C_6H_4\cdot C = N \\ C_6H_4\cdot C(OH)\cdot O \end{array} > C_6H_4$, as a yellow, flocculent precipitate, which gradually changes into the colourless *ψ*-base. *Phenanthraphenazoxonium hydrogen sulphate*, $\begin{array}{l} C_6H_4\cdot C = N \\ C_6H_4\cdot C\!:\!O(O\cdot SO_3H) \end{array} > C_6H_4$, is formed when the concentrated sulphuric acid solution of the *ψ*-base is exposed to moist air; it separates in glistening, violet-crystals, and when heated with alcoholic sulphuric acid is decomposed into *o*-aminophenol and phenanthraquinone.

The *perbromide*, $\begin{array}{l} C_6H_4\cdot C = N \\ C_6H_4\cdot C\!:\!OBr_3 \end{array} > C_6H_4$, is obtained when the *ψ*-base is treated with bromine in warm nitrobenzene solution as a green, metallic, crystalline precipitate.

ψ-Phenanthraphenazoxine, $\begin{array}{l} C_6H_4\cdot C = N \\ C_6H_4\cdot CH - O \end{array} > C_6H_4$, is formed by reduction of the *ψ*-base with stannous chloride in alcoholic hydrochloric acid solution; it crystallises in yellow needles, forms a yellow solution with green fluorescence, and is rapidly oxidised to the *ψ*-base when warmed to 80° or dissolved in concentrated sulphuric acid.

Hydroxydihydrophenanthraphenazoxine, $\begin{array}{l} C_6H_4\cdot CH\cdot N(OH) \\ C_6H_4\cdot CH \text{———} O \end{array} > C_6H_4$, is formed when the *ψ*-base is carefully warmed with phenylhydrazine; it crystallises in glistening, white sheaves of needles, is converted into the *ψ*-base when heated at 100°, forms a colourless solution in concentrated sulphuric acid, which becomes bluish-violet owing to formation of phenanthraphenazoxonium hydrogen sulphate, and on addition of a drop of dilute hydrochloric acid to the colourless alcoholic solution immediately yields *ψ*-phenanthraphenazoxine.

The paper concludes with a criticism of Hantzsch's views as to the constitution of the oxonium dyes (compare Hantzsch, this vol., i, 605). G. Y.

Substituted Rhodanic Acids and their Aldehyde Condensation Products. III. RUDOLF ANDREASCH and ARTHUR ZIPSER (*Monatsh.*, 1905, **26**, 1191—1208. Compare Abstr., 1903, i, 855; 1904, i, 444).—3-o-*Tolylrhodanic acid*, $CH_2 < \begin{array}{l} CO\cdot N\cdot C_7H_7 \\ S \text{—} CS \end{array}$, prepared by

the action of ethyl chloroacetate on ammonium *o*-tolyldithiocarbamate, or by boiling *o*-tolylthiocarbimide with thioglycollic acid in aqueous-alcoholic solution, crystallises from alcohol in white or light yellow needles, melts at 101°, and dissolves readily in alcohol, ether, glacial acetic acid, or acetone.

3-o-*Tolyl-5-benzylidenerhodanic acid*, $CHPh{:}C\Big\langle\begin{matrix}CO\cdot N\cdot C_7H_7\\ S\text{—}CS\end{matrix}$, crystallises in slender needles and melts at 171°.

3-o-*Tolyl*-5-o-*hydroxybenzylidenerhodanic acid*,

$$OH\cdot C_6H_4\cdot CH{:}C\Big\langle\begin{matrix}CO\cdot N\cdot C_7H_7\\ S\text{—}CS\end{matrix},$$

crystallises in nodular aggregates of light yellow needles, sinters at 150° and melts at 158°; it dissolves in aqueous ammonia to form a red solution which on warming yields an odour resembling that of phenylthiocarbimide.

3-p-*Tolylrhodanic acid*, $C_{10}H_9ONS_2$, prepared by the action of ethyl chloroacetate on ammonium *p*-tolyldithiocarbamate, crystallises in slender, light yellow needles and melts at 160°.

3-p-*Tolyl-5-benzylidenerhodanic acid*, $C_{17}H_{13}ONS_2$, crystallises in matted, slender, chrome-yellow needles and melts at 187·5°. 3-p-*Tolyl*-5-o-*hydroxybenzylidenerhodanic acid*, $C_{17}H_{13}O_2NS_2$, crystallises in microscopic, chrome-yellow needles, melts at 198°, and imparts a yellow colour to fats, but, owing to its insolubility in water, does not dye fibres. It dissolves in aqueous ammonia to form a red solution which, when warmed, gives an odour of tolylthiocarbimide, and on acidification yields a *substance* crystallising in slender, white needles; with ferric chloride and ammonia, the acidified solution gives an emerald-green coloration.

3-m-*Xylylrhodanic acid*, $CH_2\Big\langle\begin{matrix}CO\cdot N\cdot C_6H_3Me_2\\ S\text{—}CS\end{matrix}$, prepared by treating with ethyl chloroacetate the crystalline *product* obtained by the action of concentrated aqueous ammonia on a mixture of *m*-xylidine and carbon disulphide, forms a brownish-yellow oil, which is easily soluble in alcohol or ether. 3-m-*Xylyl-5-benzylidenerhodanic acid*, $CHPh{:}C\Big\langle\begin{matrix}CO\cdot N\cdot C_6H_3Me_2\\ S\text{—}CS\end{matrix}$, crystallises in chrome-yellow needles, melts at 171°, and is readily soluble in warm organic solvents. 3-m-*Xylyl*-5-m-*nitrobenzylidenerhodanic acid*, $NO_2\cdot C_6H_4\cdot CH{:}C\Big\langle\begin{matrix}CO\cdot N\cdot C_6H_3Me_2\\ S\text{—}CS\end{matrix}$, forms a viscid oil which crystallises in yellow needles when treated with alcohol.

3-o-*Hydroxyphenylrhodanic acid*, $CH_2\Big\langle\begin{matrix}CO\cdot N\cdot C_6H_4\cdot OH\\ S\text{—}CS\end{matrix}$, is formed by the action of ethyl chloroacetate on the crystalline *product* obtained by treating a mixture of *o*-aminophenol and carbon disulphide with concentrated aqueous ammonia. It separates from alcohol as a colourless or slightly yellowish-green, crystalline powder, commences to sinter at 160°, melts at 185°, is readily soluble in alcohol, ether, or acetone, and dissolves in aqueous alkali hydroxides to form solutions which, on acidification, yield a crystalline precipitate and with ferric chloride

and ammonia give the thioglycollic acid reaction. 3-o-*Hydroxyphenyl-5-benzylidenerhodanic acid*, $CHPh:C<\begin{matrix}CO\cdot N\cdot C_6H_4\cdot OH\\ S—CS\end{matrix}$, crystallises in golden-yellow leaflets and melts at 211°.

5-*Furfurylidenerhodanic acid*, $C_4OH_3\cdot CH:C<\begin{matrix}CO\cdot NH\\ S—CS\end{matrix}$, on slow crystallisation from alcohol, forms nodules and stellate aggregates of dark brown needles having a steel-blue lustre, commences to sinter at 204°, and decomposes without melting.

3-*Phenyl*-5-*furfurylidenerhodanic acid*, $C_4OH_3\cdot CH:C<\begin{matrix}CO\cdot NPh\\ S—CS\end{matrix}$, crystallises from glacial acetic acid in chrome-yellow needles, or in matted, hair-like needles from alcohol, and melts at 183°.

5-p-*Dimethylaminobenzylidenerhodanic acid*,

$$NMe_2\cdot C_6H_4\cdot CH:C<\begin{matrix}CO\cdot NH\\ S—CS\end{matrix},$$

separates from alcohol as a dark red, crystalline powder, commences to sinter at 200°, decomposes and melts at 246°, and dissolves in alcohol or concentrated acids to form yellow solutions.

5-p-*Dimethylaminobenzylidene*-3-*methylrhodanic acid*,

$$NMe_2\cdot C_6H_4\cdot CH:C<\begin{matrix}CO\cdot NMe\\ S—CS\end{matrix},$$

separates from alcohol as a red, shimmering, crystalline powder or in scales, melts at 220°, forms red solutions in alcohol, ether, or acetone, and dissolves in concentrated hydrochloric acid to form a yellow solution which becomes red on dilution.

5-p-*Dimethylaminobenzylidene*-3-*ethylrhodanic acid*, $C_{14}H_{16}ON_2S_2$, crystallises in dark red scales and melts at 155°.

5-p-*Dimethylaminobenzylidene*-3-*allylrhodanic acid*,

$$NMe_2\cdot C_6H_4\cdot CH:C<\begin{matrix}CO\cdot N\cdot C_3H_5\\ S—CS\end{matrix},$$

crystallises in small, scarlet leaflets and scales, melts at 131°, is slightly soluble in boiling alcohol, and dyes wool an orange-red, which is bleached by fourteen days' exposure to light.

3-*Phenyl*-5-*dimethylaminobenzylidenerhodanic acid*,

$$NMe_2\cdot C_6H_4\cdot CH:C<\begin{matrix}CO\cdot NPh\\ S—CS\end{matrix},$$

separates from alcohol as a red, crystalline powder, melts at 235°, and is most easily soluble in acetone.

3-o-*Tolyl*-5-p-*dimethylaminobenzylidenerhodanic acid*,

$$NMe_2\cdot C_6H_4\cdot CH:C<\begin{matrix}CO\cdot N\cdot C_7H_7\\ S—CS\end{matrix},$$

crystallises in yellowish-red needles having a slight blue lustre and melts at 209°.

3-p-*Tolyl*-5-p-*dimethylaminobenzylidenerhodanic acid*, $C_{19}H_{18}ON_2S_2$, crystallises in delicate, orange-yellow needles and melts at 206°.

3-m-*Xylyl*-5-p-*dimethylaminobenzylidenerhodanic acid*,

$$NMe_2\cdot C_6H_4\cdot CH:C<\begin{matrix}CO\cdot N\cdot C_6H_4Me_2\\ S—CS\end{matrix},$$

crystallises in light orange-red needles, commences to sinter at 180°, and is completely melted at 200°.

When coupled with diazo-compounds, hydroxybenzylidenerhodanic acid forms derivatives which dye silk and wool directly fast yellow or orange-yellow colours. G. Y.

Substituted Rhodanic Acids and their Aldehyde Condensation Products. IV. JOSEF STUCHETZ (*Monatsh.*, 1905, **26**, 1209—1216. Compare preceding abstract).—3-o-*Tolyl*-5-m-*nitrobenzylidenerhodanic acid*, $NO_2\cdot C_6H_4\cdot CH{:}C<\begin{matrix}CO\cdot N\cdot C_7H_7\\ S\text{—}CS\end{matrix}$, forms a chrome-yellow, crystalline powder, melts at 193°, and is readily soluble in hot alcohol or cold acetone.

3-o-*Tolyl*-5-p-*nitrobenzylidenerhodanic acid*, $C_{17}H_{12}O_3N_2S_2$, crystallises in chrome-yellow, glistening leaflets, commences to blacken at 24°, and melts at 260°.

3-o-*Tolyl*-5-p-*methoxybenzylidenerhodanic acid*,

$$OMe\cdot C_6H_4\cdot CH{:}C<\begin{matrix}CO\cdot N\cdot C_7H_7\\ S\text{—}CS\end{matrix},$$

crystallises in greenish-yellow needles, melts at 208—212°, and is sparingly soluble in hot alcohol or ether, but easily so in acetone.

3-o-*Tolyl*-5-m-*methoxybenzylidenerhodanic acid*, $C_{18}H_{15}O_3NS_2$, forms a chrome-yellow, crystalline powder and melts at 168°.

3-o-*Tolyl*-5-mp-*methylenedioxybenzylidenerhodanic acid*,

$$CH_2{:}O_2{:}C_6H_3\cdot CH{:}C<\begin{matrix}CO\cdot N\cdot C_7H_7\\ S\text{—}CS\end{matrix},$$

crystallises in greenish-yellow needles and melts at 190°.

3-o-*Tolyl*-5-*cinnamylidenerhodanic acid*,

$$CHPh{:}CH\cdot CH{:}C<\begin{matrix}CO\cdot N\cdot C_7H_7\\ S\text{—}CS\end{matrix},$$

crystallises in glistening, orange-red needles, melts at 175°, and is readily soluble in ether or acetone.

3-o-*Tolyl*-5-*furfurylidenerhodanic acid*, $C_4OH_3\cdot CH{:}C<\begin{matrix}CO\cdot N\cdot C_7H_7\\ S\text{—}CS\end{matrix}$, crystallises from alcohol in long, brown needles having a blue lustre and melts at 144°.

3-p-*Tolyl*-5-p-*nitrobenzylidenerhodanic acid*, $C_{17}H_{12}O_3N_2S_2$, forms glistening, orange-yellow scales and melts at 201°.

3-p-*Tolyl*-5-p-*methoxybenzylidenerhodanic acid*, $C_{18}H_{15}O_2NS_2$, forms a greenish-yellow, crystalline powder and melts at 170°.

3-p-*Tolyl*-5-p-*hydroxy*-m-*methoxybenzylidenerhodanic acid*,

$$C_{18}H_{15}O_3NS_2,$$

forms a yellow, crystalline powder and melts at 202°.

3-p-*Tolyl*-5-mp-*methylenedioxybenzylidenerhodanic acid*, $C_{18}H_{13}O_3NS_2$, forms a sparingly soluble, chrome-yellow, crystalline powder and melts at 197°.

3-p-*Tolyl*-5-*cinnamylidenerhodanic acid*, $C_{18}H_{14}ONS_2$, forms a dark orange-yellow powder, consisting of microscopic needles, and melts at 185°.

3-p-*Tolyl-5-furfurylidenerhodanic acid*, $C_{15}H_{12}O_2NS_2$, forms a greenish-yellow, crystalline powder, melts at 186°, and is moderately soluble in boiling alcohol. G. Y.

Action of Sulphuric Acid on Diphenylamine. VICTOR KADIERA (*Ber.*, 1905, **38**, 3575—3578. Compare Gnehm and Werdenberg, Abstr., 1900, i, 93. Ullmann, Abstr., 1903, i, 692).—When heated at 80° with 1 part of concentrated sulphuric acid and 3 parts of sulphuric acid containing 20 per cent. of anhydride, diphenylamine yields 37·5 per cent. of its weight of diphenylbenzidine, together with diphenylbenzidinesulphone.

Diphenylbenzidine, $NHPh\cdot C_6H_4\cdot C_6H_4\cdot NHPh$, crystallises from toluene in white leaflets, melts at 242° (corr.), is readily soluble in boiling toluene or acetic acid, but only sparingly so in benzene, acetone, or alcohol, and dissolves in cold concentrated sulphuric acid to form a colourless solution which becomes intensely blue when heated, or on addition of a small quantity of potassium nitrate; the yellow solution in acetic acid becomes blue on addition of potassium dichromate, greenish-yellow on addition of ferric chloride.

Diphenylbenzidinedicarboxylic acid, $C_{12}H_8(NH\cdot C_6H_4\cdot CO_2H)_2$, is formed when *o*-chlorobenzoic acid is boiled with benzidine and potassium carbonate in amyl alcohol solution, in presence of copper powder, in a reflux apparatus. It crystallises from boiling alcohol as a delicate, yellowish-green powder, melts and decomposes at 278° (corr.), and at 285° loses carbon dioxide and yields diphenylbenzidine.

Diphenylbenzidinesulphone, $$\begin{array}{l}\phantom{NHPh\cdot{}}CH\cdot CH{:}C\text{———}C\cdot CH{:}CH\\ NHPh\cdot C\text{—}CH{:}C\cdot SO_2\cdot C\cdot CH{:}C\cdot NHPh\end{array}$$, crystallises from amyl alcohol as a yellowish-brown powder, does not melt at 300°, forms solutions with slight blue fluorescence in amyl alcohol and aniline, and gives colour reactions similar to those of diphenylbenzidine. G. Y.

Coloured and Colourless Di-imines. HANS H. PRINGSHEIM (*Ber.*, 1905, **38**, 3354—3356. Compare Jackson and Calhane, Abstr., 1902, i, 645; Willstätter, *ibid.*, 1904, i, 511; this vol., i, 723).—A *résumé* of earlier work. J. J. S.

Indophenols containing the Sulphamino-group. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 160710).—Indophenols containing the sulphamino-group, of which the simplest representative has the constitution $O{:}C_6H_4{:}N\cdot C_6H_4\cdot NH\cdot SO_2Ph$, are obtained by oxidising an arylsulphonyl-*p*-phenylenediamine together with a phenol in which the para-position is free. Thus, on oxidising a mixture of toluene-*p*-sulphonyl-*p*-phenylenediamine hydrochloride and phenol with chromic acid, the *indophenol* is obtained as a reddish-brown precipitate, insoluble in water, but dissolving in alkali hydroxides or carbonates to an intensely blue solution. The phenol may be replaced by *o*- or *m*-cresol or α-naphthol, and the amine by toluene-*p*-sulphonyl-*o*-chloro-*p*-phenylenediamine or toluene-*p*-sulphonyl-*om*-tolylenediamine.

C. H. D.

Rhodamines. I. EMILIO NOELTING and KARL DZIEWOŃSKI (*Ber.*, 1905, **38**, 3516—3527).—A typical rhodamine is produced when *o'*-amino-*o*-cresol, $OH \cdot C_6H_3Me \cdot NH_2$ [2 : 1 : 6], is condensed with phthalic anhydride under the conditions which convert *m*-aminophenol into the simplest rhodamine, thus proving that the OH or NH_2 group in fluorescein and the rhodamines is in the para-position to the fundamental carbon atom.

Tetramethylrhodamine yields a *hydrochloride*, $C_{24}H_{23}O_3N_2Cl,3H_2O$, which forms green needles with a metallic lustre. The *tetramethylrhodamine base*, $C_{24}H_{22}O_3N_2,3H_2O$, is insoluble in water and in excess of alkali hydroxide, but separates from hot alcohol in green flakes with a metallic lustre; it loses water of crystallisation at 120—130°, gives a colourless solution in ether, benzene, toluene, or xylene, and separates from the latter in flat, colourless needles with C_8H_{10}, which is evolved at 130—150°, the base melting at 232°.

Tetraethylrhodamine hydrochloride, $C_{28}H_{31}O_3N_2Cl$, crystallises from dilute hydrochloric acid in scales with a metallic lustre and dissolves in alcohol very easily to a carmine-red solution with an orange-yellow fluorescence. Addition of concentrated alkali to a solution of the hydrochloride yields a reddish-white precipitate, which readily dissolves on diluting the alkali; from this solution, the *base*,

$$C_{28}H_{30}O_3N_2,4H_2O,$$

separates in glistening, green scales. It dissolves in water and in alcohol to red solutions with a green fluorescence, but yields colourless solutions in ether, benzene, xylene, &c. The green base loses water when kept in a vacuum over sulphuric acid; it becomes colourless when heated at 70—80°, melts at 95°, solidifies again, and melts at 165° to a clear red liquid. The colourless *anhydrous base* separates from absolute alcohol in large, almost colourless prisms, and melts at 165°; it separates from xylene in colourless prisms with C_8H_{10}, which is eliminated at 140—150°.

Diethylhomorhodamine hydrochloride, $C_{25}H_{25}O_3N_2Cl,3H_2O$, separates from dilute hydrochloric acid in green prisms with a metallic lustre, dissolves in alcohol with a yellow fluorescence, and becomes anhydrous when kept in a vacuum over sulphuric acid. The *base*, $C_{25}H_{24}O_3N_2$, separates from dilute alcohol in glistening, green scales with EtOH and H_2O; it gives a colourless solution in xylene and separates in red plates, with a golden lustre, containing xylene, which is lost at 170—175°, the base melting at 210°. The *acetyl* derivative,

$$C_{27}H_{26}O_4N_2,$$

separates from benzene or xylene, in small, white needles and melts at 257—260°.

The *hydrochloride* of *s*-diethylrhodamine, $C_{24}H_{23}O_3N_2Cl,3\frac{1}{2}H_2O$, forms brownish-red needles with a metallic lustre. The *base*, $C_{24}H_{22}O_3N_2,H_2O$, forms bluish-red, glistening, rhombic plates; it separates from xylene with $\frac{1}{2}H_2O$ in dark red, bulky crystals. The *diacetyl* derivative, $C_{28}H_{26}O_5N_2$, crystallises from a mixture of xylene and light petroleum in small, colourless prisms and melts at 205°.

apo*Rhodamine* (*aminofluorene*) *hydrochloride*, $C_{23}H_{20}O_3NCl,2\frac{1}{2}H_2O$, forms brownish-red needles and yields the free, colourless base, when boiled with water. The colourless base, $C_{23}H_{19}O_3N$, separates from

ether, alcohol, or benzene in large, flat, glistening, colourless needles, and from xylene in small, colourless prisms containing xylene, which is given off at 180—185°; the base melts at 197°.

T. M. L.

Action of Benzyl Chloride and *o*- and *p*-Nitrobenzyl Chlorides on Phenylhydrazine and *p*-Bromophenylhydrazine. Otto Flaschner (*Monatsh.*, 1905, **26**, 1069—1090. Compare Paal and Bodewig, Abstr., 1892, 1455; Ofner, Abstr., 1904, i, 818).—The action of 2 mols. of phenylhydrazine on 1 mol. of *o*-nitrobenzyl chloride in boiling alcoholic solution leads to the formation of *as*-phenyl-*o*-nitrobenzylhydrazine, phenyl-*o*-nitrobenzylidenehydrazine, which melts at 154° and is identical with Paal and Bodewig's *o*-nitrophenylmethaneazobenzene, and phenyl *o*-nitrobenzyl-*o*-nitrobenzylidenehydrazine, which melts at 126°. This substance, which is identical with Paal and Bodewig's bisphenyl-*o*-nitrobenzylhydrazine, is formed also by condensation of *o*-nitrobenzaldehyde with phenyl-*o*-nitrobenzylhydrazine.

When oxidised with aqueous ferric chloride under cooling, *as*-phenyl-*o*-nitrobenzylhydrazine yields the *tetrazone*,

$$NO_2\cdot C_6H_4\cdot CH_2\cdot NPh\cdot N\colon N\cdot NPh\cdot CH_2\cdot C_6H_4\cdot NO_2,$$

which crystallises in flat, yellow prisms and decomposes at 174—175° (corr.), but, when oxidised with mercuric oxide, it forms phenyl-*o*-nitrobenzylidenehydrazine.

The reduction product of phenyl-*o*-nitrobenzylidenehydrazine, which melts at 218—220° (Paal and Bodewig), is identical with phenyl-*o*-aminobenzylidenehydrazine (Gabriel and Leupold, Abstr., 1899, i, 85).

The action of *p*-nitrobenzyl chloride on phenylhydrazine in boiling alcoholic solution leads to the formation of (1) *phenyl-*p*-nitrobenzylhydrazine*, $C_{13}H_{13}O_2N_3$, which crystallises from alcohol in yellow prisms, melts at 95° (corr.), and forms a *hydrochloride* crystallising in transparent, white, quadratic prisms and decomposing at 198° (corr.); (2) *phenyl-*p*-nitrobenzyl-*p*-nitrobenzylidenehydrazine*, $C_{20}H_{16}O_4N_4$, which is formed also by the action of *p*-nitrobenzaldehyde on phenyl-*p*-nitrobenzylhydrazine, crystallises in needles, and melts at about 132° (corr.), and (3) *phenyl-*p*-nitrobenzylidenehydrazine*, $C_{13}H_{11}O_2N_3$, which is formed also by the interaction of phenylhydrazine and *p*-nitrobenzaldehyde, crystallises in needles, and melts at 159—160° (corr.).

The action of benzyl chloride on *p*-bromophenylhydrazine leads to the formation of as-p-*bromophenylbenzylhydrazine*, $C_{13}H_{13}N_2Br$, which crystallises in nodular aggregates of transparent, white needles, melts at 37°, and forms a *hydrochloride*, $C_{13}H_{13}N_2Br,HCl$, crystallising in needles and decomposing at 182° (corr.), and p-*bromophenylbenzylbenzylidenehydrazine*, $C_{20}H_{17}N_2Br$, which can be prepared from *p*-bromophenylbenzylhydrazine and benzaldehyde; it crystallises in greenish-yellow leaflets and melts at 134° (corr.).

When boiled in alcoholic solution, *o*-nitrobenzyl chloride and *p*-bromophenylhydrazine interact to form as-p-*bromophenyl*-o-*nitrobenzylhydrazine*, $C_{13}H_{12}O_2N_3Br$, which separates from alcohol in lemon-yellow crystals, melts at 123° (corr.), and forms a *hydrochloride*,

$C_{13}H_{12}O_2N_3Br,HCl$, crystallising in white needles and decomposing at about 190°, and p-*bromophenyl*-o-*nitrobenzylidenehydrazine*,

$$C_{13}H_{10}O_2N_3Br,$$

which is formed also by the action of *o*-nitrobenzaldehyde on *p*-bromophenylhydrazine; it crystallises in dark red needles and melts and decomposes at 184—189° (corr.).

p-*Bromophenyl*-o-*nitrobenzyl*-o-*nitrobenzylidenehydrazine*,

$$C_{20}H_{15}O_4N_4Br,$$

is formed by heating *o*-nitrobenzaldehyde with *as*-*p*-bromophenyl-*o*-nitrobenzylhydrazine in alcoholic solution; it crystallises in yellow needles and melts at 167° (corr.). The action of *p*-nitrobenzyl chloride on *p*-bromophenylhydrazine leads to the formation of (1) as-p-*bromophenyl*-p-*nitrobenzylhydrazine*, which crystallises in yellow prisms and melts at 144° (corr.); the *hydrochloride* forms white leaflets and decomposes at 217°; (2) p-*bromophenyl*-p-*nitrobenzyl*-p-*nitrobenzylidenehydrazine*, $C_{20}H_{15}O_4N_4Br$, which is formed also by the action of *p*-nitrobenzaldehyde on *as*-*p*-bromophenyl-*p*-nitrobenzylhydrazine; it crystallises in scarlet prisms and melts at 182—183° (corr.); and (3) p-*bromophenyl*-p-*nitrobenzylidenehydrazine*, $C_{13}H_{10}O_2N_3Br$, which is formed also from *p*-nitrobenzaldehyde and *p*-bromophenylhydrazine; it crystallises in flat, red needles and melts at 154—156° (corr.). The *as*-*sec*-hydrazine is always the chief product of the action of benzyl and nitrobenzyl chlorides on phenyl- or bromophenyl-hydrazine. G. Y.

Nitrogen Derivatives of Acetylcarbinol. F. Carlo Palazzo and A. Caldarella (*Atti R. Accad. Lincei*, 1905, [v], **14**, ii, 151—156).—The p-*nitrophenylhydrazone*,

$$OAc\cdot CH_2\cdot CMe\colon N\cdot NH\cdot C_6H_4\cdot NO_2,$$

prepared by the action of a hydrochloric acid solution of *p*-nitrophenylhydrazine on acetylcarbinyl acetate (Perkin, Trans., 1891, **59**, 786) in presence of excess of sodium acetate, separates from benzene as a yellow, crystalline powder melting at 144°. The p-*bromophenylhydrazone*, $C_{11}H_{13}O_2N_2Br$, crystallises from light petroleum, benzene, or alcohol in white scales, which melt at 137—138°, and when kept rapidly turns into a resin.

Acetylcarbinyl-p-*nitrophenylhydrazone*, $C_9H_{11}O_3N_3$, separates from xylene as a pale yellow, crystalline powder melting at 190—191°. The corresponding p-*bromophenylhydrazone*, $C_9H_{11}ON_2Br$, crystallises from light petroleum, either alone or mixed with benzene, in white leaflets melting at 128—130°. T. H. P.

Action of Secondary Asymmetric Hydrazines on Sugar. II. Rudolf Ofner (*Monatsh.*, 1905, **26**, 1165—1190. Compare Abstr., 1904, i, 689, 798, 936; this vol., i, 90, 158).—A reply to Neuberg (this vol., i, 90) and a criticism of Neuberg and Strauss' work (Abstr., 1902, ii, 676). It is probable that the body-juices examined by these authors contain dextrose and not lævulose, as the phenylmethylosazone test for the latter sugar is trustworthy only if the osazone separates in about five hours at the ordinary temperature.

G. Y.

Amines and Diazopyrroles. FRANCESCO ANGELICO (*Atti R. Accad. Lincei*, 1905, [v], **14**, ii, 167—170).—The analogy in behaviour between phenols and pyrrole derivatives is supported by the fact that on reduction nitrosophenylindole yields aminophenylindole and nitrosodiphenyl- and nitrosotriphenyl-pyrroles give the corresponding aminopyrroles. The latter behave like the aminoindoles towards nitrous acid, giving rise to extremely stable diazopyrroles.

Aminotriphenylpyrrole, $C_{22}H_{18}N_2$, prepared by reducing an alcoholic solution of nitrosotriphenylpyrrole by means of zinc dust and acetic acid, crystallises from benzene in colourless needles melting and decomposing at 183—184°.

Aminodiphenylpyrrole, $C_{16}H_{14}N_2$, crystallises from benzene in pale yellow scales melting at 187—188°.

Diazotriphenylpyrrole, $C_{22}H_{15}N_3$, crystallises from benzene or alcohol in reddish-brown needles melting and decomposing at 158—159°. Its *hydrochloride*, $C_{22}H_{15}N_3$,HCl, forms a yellow powder decomposing at about 160°.

Diazodiphenylpyrrole, $C_{16}H_{11}N_3$, crystallises from benzene in large, reddish-brown needles melting and decomposing at 122—123°; the *hydrochloride* is a yellow powder decomposing at about 173°.

T. H. P.

Derivatives of 2-Picolyl- and of 2-Picolylmethyl-alkine. III. KARL LÖFFLER and M. KIRSCHNER (*Ber.*, 1905, **38**, 3329—3343. Compare Abstr., 1904, i, 265, 616).—2-*β*-2′-*Pipecolylethylpyridine*, $C_5NH_4\cdot C_2H_4\cdot C_5NH_9Me$, is obtained when 2-picolylalkine bromide is heated with twice its weight of 2-pipecoline and ethyl alcohol at 100° for 5—6 hours. It is a viscid, colourless oil, distils at 152° under 15 mm. pressure, has a sp. gr. 1·0105 at 15°, dissolves readily in most organic solvents, and its aqueous solution is strongly alkaline. It cannot be resolved into active components by means of *d*-tartaric acid or camphorsulphonic acid. The *hydrochloride*, $C_{13}H_{20}N_2$,2HCl, melts at 175°, the *aurichloride* melts and decomposes at 190°, the *platinichloride*, $C_{13}H_{20}N_2,H_2PtCl_6$, crystallises in pale yellow plates and decomposes at 230—232°, the *picrate* melts at 131—132°, and the *mercurichloride* at 118°.

2-Picolylmethylalkine (Ladenburg, *Annalen*, 1898, **301**, 124), when heated for 12—14 hours at 125° with hydrobromic acid saturated at 0°, yields 1-*β*-*bromopropylpyridine hydrobromide*,

$$C_5NH_4\cdot CH_2\cdot CHBr\cdot CH_3,HBr.$$

The *base* is a yellow oil with an intense odour, and is sparingly soluble in water. The *picrate* crystallises from water in plates and melts at 105°; the *platinichloride* melts at 170° and the *aurichloride* at 102—103°. When warmed or when kept, the base undergoes intramolecular transformation into the *pyridinium bromide*, $\begin{array}{l}CH{:}CH\cdot C{-\!\!-}CH_2\\ \vert \qquad\quad \Vert \qquad \vert \\ CH{:}CH\cdot NBr\cdot CHMe\end{array}$, which crystallises from ethyl acetoacetate in colourless plates melting at 162°, and readily soluble in alcohol, chloroform, or acetone. The *iodide* melts at 147°, the *chloride* is hygroscopic and melts at 122°, and the *platinichloride* forms reddish-yellow needles melting at 188°.

2-*β*-*Diethylaminopropylpyridine*, $C_5NH_4\cdot CH_2\cdot CHMe\cdot NEt_2$, obtained by the action of diethylamine on the corresponding bromo-derivative

at 120—125°, is an oil which distils at 122° under 12 mm. pressure. It dissolves readily in most solvents, the *picrate* melts at 108°, the *platinichloride*, $C_{12}H_{20}N_2,H_2PtCl_6$, crystallises in orange-yellow needles and melts at 190°, the *aurichloride* melts at 160°, and the *mercurichloride* at 110°.

2-*β*-*Ethylaminopropylpyridine*, $C_5NH_4 \cdot CH_2 \cdot CHMe \cdot NHEt$, distils at 108—109° under 13 mm. pressure, has a sp. gr. 0·9533, darkens in contact with air, and is extremely hygroscopic. The *platinichloride* crystallises in red, well-developed prisms melting and decomposing at 225°. The *aurichloride* melts at 204°, the *mercurichloride* at 146°, and the *picrate* at 178°. The base yields a *nitroso*-derivative in the form of a red oil, which is soluble in mineral acids and which yields a *platinichloride* crystallising in orange-yellow needles and melting at 198°.

2-*β*-*Aminopropylpyridine*, $C_5NH_4 \cdot CH_2 \cdot CHMe \cdot NH_2$, distils at 103—104° under 13 mm. pressure and has a sp. gr. 1·004 at 15°. It cannot be resolved by means of tartaric or camphorsulphonic acid. The *aurichloride* melts and decomposes at 216° and the *platinichloride* at 239°. The *mercurichloride* melts at 122° and the *picrate* at 210—211°.

The bromide obtained by the action of hydrobromic acid on 2-pipecolylalkine also reacts with bases. 2-*β*-*Diethylaminoethylpiperidine*, $C_5NH_{10} \cdot CH_2 \cdot CH_2 \cdot NEt_2$, is a colourless oil distilling at 113—115° under 15 mm. pressure and has a sp. gr. 0·8288 at 15°. The *platinichloride* crystallises in glistening, yellow plates decomposing at 224°. The *hydrochloride*, $C_{11}H_{24}N_2,2HCl$, melts at 256—258°, the *hydrobromide* at 236°, the *aurichloride* at 193°, the *picrate* at 73°, and the *cadmium* salt at 163°.

2-*β*-*Ethylaminoethylpiperidine*, $C_5NH_{10} \cdot CH_2 \cdot CH_2 \cdot NHEt$, is a colourless, basic oil distilling at 95—96° under 10 mm. pressure. The *aurichloride* melts at 186°, the *platinichloride* decomposes at 196°, and the *picrate* crystallises in pale yellow needles melting at 170°. *Amino-2-ethylpiperidine* is not prepared so readily as its ethyl derivatives. It distils at 106—107° under 10 mm. pressure and its aqueous solution is strongly alkaline. The *picrate* and *mercurichloride* are oils.

2-Pipecolylmethylalkine also reacts with fuming hydrobromic acid and phosphorus at 145—150°, yielding the *hydrobromide* of the *bromo-base*, $C_5NH_{10} \cdot CH_2 \cdot CHBr \cdot CH_3$. The hydrobromide melts at 148—150° and the *hydrochloride* at 135—136°. The *aurichloride* and *picrate* are oils. The bromo-base reacts with amines.

2-*β*-*Diethylaminopropylpiperidine*, $C_5NH_{10} \cdot CH_2 \cdot CHMe \cdot NEt_2$, is a colourless oil distilling at 113—115° under 14 mm. pressure and readily soluble in alcohol or ether. It has a sp. gr. 0·8954. The *platinichloride*, $C_{12}H_{26}N_2,H_2PtCl_6$, melts and decomposes at 208°; the *aurichloride* melts at 180—181° and the *picrate* is an oil.

Conhydrine also reacts with fuming hydrobromic acid and red phosphorus at 140—150°, yielding the *hydrobromide*, $C_8H_{16}NBr,HBr$, which crystallises from alcohol in colourless needles melting at 183—185°. The *base* is oily and has an alliaceous odour. The *picrate* and *aurichloride* are oils; the *platinichloride* melts and decomposes at 182°. When heated with excess of diethylamine, the bromo-base yields *diethylaminoconiine*, $C_5NH_{10} \cdot C_3H_6NEt_2$, which distils at

112—115° under 13 mm. pressure and has a sp. gr. 0·8970 at 15° and $[\alpha]_D$ −5·82°. It closely resembles the inactive base obtained from the bromo-derivative of pipecolylmethylalkine. The *platinichloride* decomposes at 227° and the *aurichloride* at 181°. The *picrate* and *cadmium* salt are oils.

Ethylaminoconiine distils at 105° under 16 mm. pressure, has a sp. gr. 0·9001 at 15°, and is inactive. The *aurichloride* melts at 156—157°; the *platinichloride* melts and decomposes at 221—222°; the *picrate* is extremely readily soluble in alcohol. *Aminoconiine* distils at 95—99° under 15 mm. pressure, has a sp. gr. 0·9942 at 15°, and $[\alpha]_D$ − 2·33°. Hofmann and Lellmann's ε-coniceine (Abstr., 1885, 401; 1890, 1328) is obtained as a by-product in the action of amines on the bromide from conhydrine. It has $[\alpha]_D$ +37°. An inactive isomeride is also formed by the action of diethylaniline on the bromide from 2-pipecolylmethylalkine. J. J. S.

Diazoindoles. V. Castellana and Antonino d'Angelo (*Atti R. Accad. Lincei*, 1905, [v], **14**, ii, 145—151. Compare Angeli and d'Angelo, Abstr., 1904, i, 537, and Angeli, *Gazzetta*, 1893, **23**, ii, 345).—On reduction with zinc dust and acetic acid, the ethyl derivative of 3-nitroso-2-phenylindole gives 3-amino-2-phenylindole, which with nitrous acid yields diazophenylindole. The ethyl derivative of 3-nitrophenylindole or of 3-nitromethylindole, on the other hand, yields 1-ethylaminophenylindole or 1-ethylaminomethylindole, and no diazo-compound is obtained with nitrous acid, because no hydrogen is attached to the carbon atom bearing the amino-group and no mobile hydrogen to the nitrogen atom. It is hence assumed that, when the diazo-compound is obtained, the aminophenylindole behaves as the tautomeride having the structure $C_6H_4{<}{\overset{CH(NH_2)}{\underset{N}{\rule{3em}{0.4pt}}}}{>}CPh$. These diazo-compounds are very stable, probably owing to the diazo-group being between two substituents in the ortho-position.

3-*Nitroso-2-phenylindole ethyl ether*, $C_{16}H_{14}ON_2$, crystallises from light petroleum in orange-red needles melting at 91°.

Diazophenylindole, $C_{14}H_9N_3$, crystallises from light petroleum in intensely orange-yellow, unstable prisms having a characteristic odour and melting at 115°. The *picrate*, $C_{20}H_{12}O_7N_6$, crystallises from alcohol in yellow needles melting and decomposing at 155°; the *hydrochloride*, $C_{14}H_9N_3,HCl$, forms yellow needles melting at 173°; the *nitrate*, $C_{14}H_9N_3,HNO_3$, separates from water in crystals decomposing at 164—165°; the *chromate*, $C_{14}H_9N_3,CrO_3$, separates from water in large, yellow crystals melting at about 255°. On reduction in ethereal solution with aluminium amalgam, diazophenylindole yields nitrosophenylindole, and by prolonged boiling with 25 per cent. sulphuric acid solution it is converted into *azophenylindole*,

$$N{<}{\overset{C_6H_4}{\underset{CPh}{}}}{>}C{:}N{\cdot}N{:}C{<}{\overset{C_6H_4}{\underset{CPh}{}}}{>}N,$$

which crystallises from xylene in yellowish-red scales decomposing at about 180°, and on reduction yields aminophenylindole.

Reduction of the ethyl derivative of 3-nitro-2-methylindole yields a

compound which does not give a diazo-compound on treatment with nitrous acid, but forms a *picrate*, $C_{17}H_{17}O_7N_5$, melting at 180—182°.

Diazomethylindole, $C_9H_7N_3$, separates from light petroleum in dark yellow, unstable crystals melting at 94°. Its *picrate*, $C_{15}H_{10}O_7N_6$, crystallises from alcohol in yellow needles melting at 172°; its *iodide*, $C_9H_7N_3I_2$, forms a brown, crystalline precipitate decomposing at about 80°; the *hydrochloride*, $C_9H_7N_3,2HCl$, is obtained as a brown, crystalline precipitate decomposing at about 100°. T. H. P.

Pyrazoline Ketones. E. Azzarello (*Atti R. Accad. Lincei*, 1905, [v], **14**, ii, 229—234. Compare von Pechmann, Abstr., 1894, i, 438; 1895, i, 328; 1899, i, 232; 1901, i, 167, 168).—By the action of diazomethane on unsaturated ketones containing the group ·CH:CH·CO· or ·CH:CH·CO·CH:CH·, the following compounds have been obtained.

5(or 3)-*Acetyl-4-phenylpyrazoline*, $CH{<}^{CHPh}_{N\cdot NH}{>}CHAc$, prepared by the action of diazomethane on benzylideneacetone in ethereal solution, crystallises from alcohol in white needles melting at 105—106° and is soluble in chloroform, ether, acetone, or benzene, and slightly so in light petroleum or water; it turns red in the air, decolorises alkaline permanganate solution instantly, gives red colorations with acids, is resinified by picric acid in alcoholic solution, and, in alcoholic solution containing a little water, forms more or less unstable precipitates with platinic or mercuric chloride or ammoniacal silver nitrate solution. The *oxime*, $C_3H_4N_2Ph\cdot CMe:N\cdot OH$, separates in minute, shining crystals melting at 181—182°, dissolves in alcohol, ether, or acetone, and with concentrated sulphuric acid gives a violet-red coloration with yellow edges. Oxidation of 5(or 3)-acetyl-4-phenylpyrazoline in chloroform solution with bromine and subsequently with potassium permanganate yields 4-phenylpyrazole-5(or 3)-carboxylic acid (compare Knorr, Abstr., 1895, i, 396) and Pechmann (*loc. cit.*).

Phenylpyrazoline ketone, $CO(C_3H_4N_2Ph)_2$, prepared by the interaction of dibenzylideneacetone and diazomethane in ethereal solution, is a yellow substance melting at 214—216°, and is mixed with a small quantity of a yellow, crystalline, isomeric compound melting at 174—176°. T. H. P.

Transformation of Pyrroles into Derivatives of Pyrazole. V. Castellana (*Atti R. Accad. Lincei*, 1905, [v], **14**, ii, 242—244).—On boiling an alcoholic solution of benzeneazo-2:5-dimethylpyrrole for some hours with sodium hydroxide and hydroxylamine, it yields a *compound*, $C_{12}H_{13}ON_3$, which crystallises from benzene in minute, yellow needles melting at 175°. Its *benzoyl* derivative, $C_{19}H_{17}O_2N_3$, separates from light petroleum in yellow crystals melting at 156°. On boiling the compound with dilute sulphuric acid solution, it is converted into a *ketone*, $\begin{matrix}CMe{:}CH\\ \vert \qquad\\ NPh{-}N\end{matrix}{>}C\cdot COMe$ (?), which crystallises from light petroleum in long, almost white needles melting at 90°.

The compound $C_{12}H_{13}ON_3$ has probably the constitution

$$\begin{matrix}\text{CMe:CH} \\ | \\ \text{NPh—N}\end{matrix}\!>\!\text{C·CMe:N·OH},$$

so that hydroxylamine acts on benzeneazo-2 : 5-dimethylpyrazole in the same manner as it does on the pyrroles and nitrosopyrroles.

T. H. P.

1-Phenyl-4-methylpyrazolone. Friedrich Stolz (*Ber.*, 1905, 38, 3273—3276. Compare Michael, this vol., i, 564)—1-Phenyl-4-methyl-5-pyrazolone, melting at 148°, is formed from 1-phenyl-4-methyl-5-pyrazolone-3-carboxylic acid by removal of carbon dioxide. In Fichter, Enzenauer, and Uellenberg's paper (Abstr., 1900, i, 312), the nomenclature of the 1-phenyl-4-methyl-5-pyrazolone and 1-phenyl-4-methyl-3-pyrazolone must be interchanged; the substance termed 2-acetyl-1-phenyl-4-methyl-3-pyrazolone, and melting at 167°, is 5-acetoxy-1-phenyl-4-methylpyrazole. A number of 1-phenyl-5-pyrazolone and the corresponding 1-phenyl-3-pyrazolone derivatives are quoted to show that the latter melt always at the higher temperature. When heated with methyl iodide and methyl alcohol in a sealed tube for six hours in the water-bath, 1-phenyl-4-methyl-5-pyrazolone forms 1-*phenyl*-2 : 4-*dimethyl*-5-*pyrazolone*, $C_{11}H_{12}ON_2$, which crystallises from benzene in colourless prisms, or from water in glistening prisms containing $2H_2O$, melts when anhydrous at 125°, is less soluble in water than is antipyrine, and forms precipitates with picric acid and ferrocyanic acid; it is obtained also by decomposition of methylantipyrine.

G. Y.

5-Methylpyrimidine. Otto Gerngross (*Ber.*, 1905, 38, 3394—3408).—Details are given for preparing *C*-methylbarbituric acid from ethyl *iso*succinate. 2 : 4 : 6-*Trichloro-5-methylpyrimidine*, $\text{CCl}\!<\!\begin{matrix}\text{N·CCl}\\\text{N:CCl}\end{matrix}\!>\!\text{CMe}$, prepared by heating the sodium derivative of methylbarbituric acid with phosphorus oxychloride for 2—3 hours at 120°, crystallises from water in thin, rhombic plates, melts at 67·5—68°, boils at 245·5° under 748 mm. pressure, and when heated with zinc dust and water gives rise to a mixture of 5-*methylpyrimidine*, $\text{CH}\!<\!\begin{matrix}\text{N·CH}\\\text{N:CH}\end{matrix}\!>\!\text{CMe}$, and 2-*chloro*-5-*methylpyrimidine.* The former crystallises in flat, lustrous needles, melts at 30·5°, boils at 151·5° under 735 mm. pressure, and gives a *mercurichloride* melting at 246°, a *picrate* melting at 141°, and an *aurichloride* which melts at 209°. 2-*Chloro*-5-*methylpyrimidine* crystallises from water in soft, colourless needles, melts at 92·5°, and gives a *mercurichloride* melting at 219°; its structure follows from its giving 2-*amino*-5-*methylpyrimidine*, $\text{NH}_2\text{·C}\!<\!\begin{matrix}\text{N·CH}\\\text{N:CH}\end{matrix}\!>\!\text{CMe}$, when heated with alcoholic ammonia for three hours at 200°. This substance crystallises from hot water in four-sided prisms, melts at 193·5°, gives a *platinichloride* which decomposes at 255°, and may be synthesised as follows. iso*Succinylguanidine*, $\text{NH}_2\text{·C}\!<\!\begin{matrix}\text{N·C(OH)}\\\text{N:C(OH)}\end{matrix}\!>\!\text{CMe}$, obtained by condensing ethyl

*iso*succinate with guanidine thiocyanate by means of sodium in absolute alcohol, crystallises from water in thin, rhombic, nacreous plates, does not melt at 300°, and when heated with phosphorus oxychloride gives 4 : 6-*dichloro-2-amino-5-methylpyrimidine*; this sublimes in a vacuum in well-formed prisms, melts at 249°, and on reduction with zinc dust and water gives the 2-amino-5-methylpyrimidine described above.

Ammonia at the ordinary temperature converts 2 : 4 : 6-trichloro-5-methylpyrimidine dissolved in absolute alcohol into 2 : 4-*dichloro-6-amino-5-methylpyrimidine*, which crystallises from water in long, thin needles, melts at 201°, and can be sublimed; it is not reduced when boiled with zinc dust and water, but with hydriodic acid readily gives 6-*iodo-4-amino-5-methylpyrimidine*, which crystallises from water in thin, four-sided plates, melts at 238°, and gives a *hydriodide* melting at 227°. On reduction with zinc dust and water, 4-*amino-5-methylpyrimidine* is obtained, which melts at 176° and gives a *picrate* melting at 219—221°. 4 : 6-*Diamino-5-methylpyrimidine* is obtained by heating 6-iodo-4-amino-5 methylpyrimidine with alcoholic ammonia for three hours at 210°; it is purified by distillation in a vacuum, melts at 243°, and crystallises from water in large, colourless needles; the *hydrochloride* sublimes in a vacuum, the *platinichloride* decomposes at 265—266°, and the *nitrate* decomposes at 276°.

6-*Chloro-2 : 4-diamino-5-methylpyrimidine* is prepared by heating 2 : 4 : 6-trichloro-5-methylpyrimidine with alcoholic ammonia at 160°; it crystallises from water in quadrangular plates, melts at 199—200°, and gives a *nitrate* which decomposes at 202° and a crystalline *platinichloride* which decomposes at 300°. The same base is obtained by heating either 4 : 6-dichloro-2-amino-5-methylpyrimidine or 2 : 6-dichloro-4-amino-5-methylpyrimidine with alcoholic ammonia at 160°.

On reduction with boiling hydriodic acid and red phosphorus, 2 : 4-*diamino-5-methylpyrimidine* is formed; it crystallises from alcohol or ethyl acetate in aggregates of large prisms, melts at 188—189°, and gives a *nitrate* which decomposes at 231° and a *platinichloride* which decomposes at 246°.

2 : 4 : 6-*Triamino-5-methylpyrimidine* is obtained by heating 2 : 4 : 6-trichloro-5-methylpyrimidine with alcoholic ammonia at 200°; it melts at 227—228° and gives a *nitrate*, $C_5H_9N_5,2HNO_3$, which decomposes between 168° and 178°; the *platinichloride* has the composition $C_5H_9N_5,H_2PtCl_6$. W. A. D.

A Synthesis of Thymine. OTTO GERNGROSS (*Ber.*, 1905, 38, 3408—3411).—6-*Chloro-2 : 4-dimethoxy-5-methylpyrimidine*, prepared by the action of methyl alcohol and sodium methoxide on 2 : 4 : 6-trichloro-5-methylpyrimidine (preceding abstract), crystallises from light petroleum in flat needles, melts at 76—77°, and when reduced with zinc dust and alcohol gives 2 : 4-*dimethoxy-5-methylpyrimidine.* This crystallises from light petroleum in flat needles, melts at 60°, and boils at 322° under 758 mm. pressure; the *platinichloride* melts and decomposes at 185°. On heating the base with concentrated hydrochloric acid on the water-bath, thymine (2:4-dihydroxy-5-methylpyrimidine) is obtained identical with the natural base. W. A. D.

Condensation Products of Alloxan with Saturated Ketones. OTTO KÜHLING (*Ber.*, 1905, **38**, 3003—3007).—Alloxan condenses with acetophenone, ethoxyacetophenone, and dibenzyl ketone, in the presence of hydrogen chloride, in aqueous-alcoholic solution cooled by ice.

Phenacyldialuric acid, $COPh\cdot CH_2\cdot C(OH)<\begin{smallmatrix}CO\cdot NH\\CO\cdot NH\end{smallmatrix}>CO,H_2O$, formed from alloxan and acetophenone, crystallises from boiling water in small, white needles, melts and decomposes at 212°, and is moderately soluble in hot water, alcohol, acetone, or glacial acetic acid. It forms an amorphous, white precipitate with silver nitrate in neutral solution, reacts with bromine in warm glacial acetic acid solution, forming a *substance* which crystallises in white needles and melts at 214°, and when shaken with benzoyl chloride in dilute sodium hydroxide solution yields *phenacylalanturic acid*, $COPh\cdot CH_2\cdot C(OH)<\begin{smallmatrix}NH\cdot CO\\CO-NH\end{smallmatrix}$, which crystallises from water in white needles and melts and decomposes at 159°. The *acetyl* derivative, $C_{14}H_{12}O_6N_2$, formed by boiling phenacyldialuric acid with acetic anhydride, separates from aqueous acetone in white crystals, melts and decomposes at 226—227°, and is soluble in aqueous sodium carbonate.

p-*Ethoxyphenacyldialuric acid*, $C_{14}H_{14}O_6N_2$, formed from *p*-ethoxyacetophenone and alloxan, crystallises in small, white leaflets, melts and decomposes at 214°, and is easily soluble in acetone.

αγ-Diphenylacetonyldialuric acid,

$$CH_2Ph\cdot CO\cdot CHPh\cdot C(OH)<\begin{smallmatrix}CO\cdot NH\\CO\cdot NH\end{smallmatrix}>CO,$$

from dibenzyl ketone and alloxan, separates from boiling alcohol in white, crystalline aggregates, melts and decomposes at 233°, and is sparingly soluble in water or acetone. G. Y.

Quinazoline. III. SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1905, **38**, 3559—3562. Compare Abstr., 1903, i, 445; 1904, i, 1060; Gabriel and Stelzner, Abstr., 1896, i, 506).—Dihydroquinazoline is obtained in a yield of 25 per cent. of the theoretical by boiling 4-chloroquinazoline with hydrogen iodide in glacial acetic acid solution, adding water, and treating the periodide so formed with sulphur dioxide in aqueous solution. When boiled with phosphorus oxychloride and poured on to ice, 4-hydroxy-6-methylquinazoline, melting at 255° (m. p. 251°; Ehrlich, Abstr., 1902, i, 25), and 4-oxy-8-methylquinazoline (Findeklee, *Ber.*, 1905, **38**, 3555) yield 4-*chloro*-6-*methylquinazoline*, $C_6H_3Me<\begin{smallmatrix}N=CH\\CCl:N\end{smallmatrix}$, melting at 107—108°, and 4-*chloro*-8-*methylquinazoline*, melting at 130°, respectively. These crystallise from light petroleum in needles, and when treated with fuming hydriodic acid are reconverted into the oxy-compounds.

Potassium *o*-carbamidobenzoate, formed when an aqueous solution of anthranilic acid and potassium cyanate is evaporated to dryness on the water-bath, is converted into 2 : 4-dioxyquinazoline when evaporated with hydrochloric acid. 2 : 4-Dichloroquinazoline is formed when the dioxy-compound is boiled with phosphorus pentachloride and

oxychloride in a reflux apparatus. It is reduced by fuming hydriodic acid and phosphonium iodide at 50—60° with formation of 4-hydroxyquinazoline, but when treated with hydrogen iodide in glacial acetic acid it yields dihydroquinazoline in a yield of 43 per cent. of the theoretical. G. Y.

Synthesis of 5-Nitro-4-keto-2-methyldihydroquinazolines from 6-Nitroacetylanthranil and Primary Amines. Marston T. Bogert and Harvey Ambrose Seil (*J. Amer. Chem. Soc.*, 1905, **27**, 1305—1310).—Bogert and Chambers (this vol., i, 612) have shown that 6-nitroacetylanthranil readily condenses with primary amines to form quinazolines. The quinazolines obtained with methylamine, ethylamine, *n*- and *iso*propylamines, *iso*- and *sec*-butylamines, *iso*amylamine, and allylamine are now described. These compounds are white, crystalline solids, sparingly soluble or insoluble in water, carbon tetrachloride, carbon disulphide, light petroleum, cold benzene, or cold ether, moderately soluble in the two last-mentioned solvents at the boiling point and in cold methyl, ethyl, or amyl alcohol or acetone, but easily soluble in chloroform, ethyl acetate, hot alcohol, or hot acetone.

5-Nitro-4-keto-2-methyldihydroquinazoline, obtained by Bogert and Chambers (*loc. cit.*) from 6-nitroacetylanthranil and ammonia, is freely soluble in alkalis, moderately so in water, and in these respects differs from the quinazolines now described. 6-*Nitroacetylanthranilamide*, $NO_2 \cdot C_6H_3(NHAc) \cdot CO \cdot NH_2$, formed as an intermediate product in this condensation, is a white, crystalline substance which melts at 218—219° (corr.), is soluble in dilute alkali, and when heated in alkaline solution is converted into the quinazoline.

5-*Nitro*-4-*keto*-2 : 3-*dimethyldihydroquinazoline*,

$$\begin{array}{l}\mathrm{CH{\cdot}CH{=\!=}C{\cdot}N{=}CMe}\\ \mathrm{CH{\cdot}C(NO_2){:}C{\cdot}CO{\cdot}NMe}\end{array},$$

from 6-nitroacetylanthranil and methylamine, melts at 203° (corr.). 5-*Nitro*-4-*keto*-2-*methyl*-3-*ethyldihydroquinazoline*,

$$\begin{array}{l}\mathrm{CH{\cdot}CH{=\!=}C{\cdot}N{=}CMe}\\ \mathrm{CH{\cdot}C(NO_2){:}C{\cdot}CO{\cdot}NEt}\end{array},$$

from 6-nitroacetylanthranil and ethylamine, melts at 208° (corr.). 5-*Nitro*-4-*keto*-2-*methyl*-3-n-*propyldihydroquinazoline* and the corresponding iso*propyl* derivative melt at 204—205° (corr.) and 219—220° (corr.) respectively. 5-*Nitro*-4-*keto*-2-*methyl*-3-iso*butyldihydroquinazoline* and the corresponding sec.-*butyl* derivative melt at 202—203° (corr.) and 209—210° (corr.) respectively. 5-*Nitro*-4-*keto*-2-*methyl*-3-iso*amyldihydroquinazoline* melts at 213—214° (corr.). 5-*Nitro*-4-*keto*-2-*methyl*-3-*allyldihydroquinazoline* is dimorphous, crystallising in rhombic plates or long needles, and melts at 160—161° (corr.).

A comparison has been made of various methods of preparing 6-nitroacetylanthranil, and the results are recorded. E. G.

Synthesis of 7-Nitro-4-keto-2-alkyldihydroquinazolines from 4-Nitroacetylanthranilic Acid and from 4-Nitroacetylanthranil. Marston T. Bogert and S. H. Steiner (*J. Amer. Chem. Soc.*, 1905, **27**, 1327—1331).—The methods of preparation of 4-nitro-2-

acetylaminobenzoic acid (Wheeler and Barnes, Abstr., 1898, i, 368) are compared. When this acid is boiled for 5—10 minutes with excess of acetic anhydride, 4-*nitroacetylanthranil*, $NO_2 \cdot C_6H_3 < \begin{matrix} CO \\ | \\ NAc \end{matrix} >$, is produced, which crystallises in pale green cubes, melts at 137—138° (corr.), is readily hydrolysed by moisture, and condenses with primary amines to form substituted anthranilamides and quinazolines. 4-*Nitro-2-acetylaminobenzamide*, $NO_2 \cdot C_6H_3(NHAc) \cdot CO \cdot NH_2$, obtained by the action of ammonia on 4-nitroacetylanthranil, crystallises in pale yellow needles, is easily soluble in hot alcohol, fairly so in ammonia, and sparingly so in acetic acid; when heated, it melts at 218—223° (corr.) and becomes converted into the quinazoline.

7-*Nitro-4-keto-2-methyldihydroquinazoline*,

$$\begin{matrix} C(NO_2) \cdot CH \colon C \cdot N = CMe \\ \| \qquad\qquad | \qquad\quad | \\ CH —— CH \colon C \cdot CO \cdot NH \end{matrix},$$

obtained by heating ammonium 4-nitroacetylanthranilate at 225°, or by the action of ammonia on 4-nitroacetylanthranil, crystallises in long, pale green needles, melts at 275—277° (corr.), and is soluble in hot water, hot alcohol, or alkalis, and slightly so in acetic acid or hot ethyl acetate; the *hydrochloride* forms silky, greenish-white needles.

7-*Nitro-4-keto-2 : 3-dimethyldihydroquinazoline*,

$$\begin{matrix} C(NO_2) \cdot CH \colon C \cdot N = CMe \\ \| \qquad\qquad | \qquad\quad | \\ CH —— CH \colon C \cdot CO \cdot NMe \end{matrix},$$

obtained by warming 4-nitroacetylanthranil with an aqueous solution of methylamine, forms light yellowish-green crystals, melts at 144—145° (corr.), and is soluble in alcohol. E. G.

Compounds of Azines of the Anthraquinone Series [with Formaldehyde]. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 159942).—The azines of the anthraquinone series (this vol., i, 720, 797) combine with formaldehyde in concentrated sulphuric acid solution below 50°. The new products, the constitution of which is unknown, are blue dyes more readily soluble and of greener shade than the parent substances. They dissolve in hot aniline or pyridine to bluish-green solutions, and in concentrated sulphuric acid to olive-brown solutions. C. H. D.

Condensation of *iso*Nitrosoketones with Aldoximes. Formation of Oxadiazines. I. OTTO DIELS and RUDOLF VAN DER LEEDEN (*Ber.*, 1905, **38**, 3357—3371).—When diacetylmonoxime is heated with either anhydrous or aqueous hydrogen chloride, the products are the dioxime and a compound, $C_6H_{10}O_2N_2,HCl$. The base, $C_6H_{10}O_2N_2$, may be obtained by the direct condensation of diacetylmonoxime with acetaldoxime at 50—60°, and the reaction appears to be characteristic of aldoximes, since benzaldoxime yields a similar base, $C_{11}H_{12}O_2N_2$. The mode of formation and general properties harmonise best with the constitutional formula, $O < \begin{matrix} N \colon CMe \\ CR \colon N \end{matrix} > CMe \cdot OH$.

4-*Hydroxy-3 : 4 : 6-trimethyl-1 : 2 : 5-oxadiazine*,

$$O < \begin{matrix} N \colon CMe \\ CMe \colon N \end{matrix} > CMe \cdot OH,$$

crystallises from hot water in flat needles, melts and decomposes at 203°. Ten c.c. of the hot saturated solution contain 1·7 grams of base. The solution is neutral, gives a red coloration with ferric chloride, and reduces silver and platinum salts on heating, but not Fehling's solution. It dissolves readily in dilute acids, and concentrated nitric acid decomposes it yielding diacetyl ; it dissolves in concentrated sulphuric acid, but is not decomposed by this reagent even at 150°. The *hydrochloride* crystallises from acetone in long prisms melting at 131°, and readily soluble in water, alcohol, or chloroform. The *sulphate*,

$$(C_6H_{10}O_2N_2)_2,H_2SO_4,$$

crystallises from alcohol in prisms and melts at 168°. The *sodium* salt, $C_6H_9O_2N_2Na,4\frac{1}{2}H_2O$, crystallises from hot alcohol in needles. Methyl iodide reacts with the base yielding the *periodide*,

$$O{<}\begin{matrix}N\text{=====}CMe\\CMe{:}NMeI(I_2)\end{matrix}{>}CMe{\cdot}OMe,$$

which crystallises from methyl alcohol in deep reddish-brown needles melting at 112° after sintering at 108—110°.

4-*Hydroxy*-6-*phenyl*-3 : 4-*dimethyl*-1 : 2 : 5-*oxadiazine*, obtained by the action of benzaldehyde on a mixture of hydroxylamine hydrochloride and diacetylmonoxime, crystallises from methyl alcohol, becomes brown at 210°, and melts and decomposes at 220°. It dissolves sparingly in most organic solvents with the exception of acetic acid, from which it crystallises in glistening needles having the composition

$$2C_{11}H_{12}O_2N_2,C_2H_4O_2.$$

When oxidised with nitric acid, the base yields benzoic acid, and when decomposed by hydrochloric acid at 180°, benzaldehyde. The *hydrochloride* crystallises from hot acetone in colourless needles melting at 146°.

With methyl iodide, it yields a mixture of products, from which the *periodide*, $C_{13}H_{17}O_2N_2I_3$, has been isolated ; this crystallises from methyl alcohol in dark reddish-brown needles melting at 126°. J. J. S.

Action of Sulphurous Acid on the Triphenylmethane Dyes. KARL DÜRRSCHNABEL and HUGO WEIL (*Ber.*, 1906, **38**, 3492—3493).—An *acid sulphite* of *p*-rosaniline, having the composition

$$HO{\cdot}C(C_6H_4{\cdot}NH_2)_3,H_2SO_3,$$

is obtained in pale red crystals by suspending rosaniline in water, passing in sulphur dioxide until the dye dissolves to an orange-yellow solution, driving off the excess of sulphur dioxide by heating until the red colour reappears, and allowing the solution to cool ; the salt is sparingly soluble in water, and on heating at 90° loses water and passes from the carbinol into the quinonoid salt.

The *normal sulphite*, $(C_{19}H_{17}N_3)_2,H_2SO_3$, of *p*-rosaniline was obtained by suspending the preceding compound in water and heating until the solution became red and metallic crystals with a green lustre were produced. The salt is very stable, is not altered by heating at 160°, and is not decomposed by prolonged heating with sodium carbonate solution : sodium hydroxide, however, converts it into rosaniline.

Triaminotriphenylcarbinol-leucosulphonic acid, $C_{19}H_{19}N_3SO_3,3\frac{1}{2}H_2O$, separates slowly from a saturated solution of *p*-rosaniline in sulphurous acid and forms yellow, minute crystals which slowly lose a part of

their water of crystallisation. Unlike the acid sulphite, this compound can be momentarily dissolved in very dilute sodium carbonate solution, but soon deposits the normal sulphite.

A solution of crystal-violet in sulphurous acid deposits a *compound*, $C_{25}H_{31}N_3SO_3,2\frac{1}{2}H_2O$, in pale violet crystals which slowly lose water of crystallisation and pass into the intensely coloured quinonoid salt.

The corresponding compound from malachite-green,

$$C_{23}H_{26}N_2SO_3,2\tfrac{1}{2} \text{ or } 1H_2O,$$

forms in the fresh state, pale green crystals which soon develop an intense green colour. T. M. L.

Salts of the Crystal-violet Group. Julius Sand (*Ber.*, 1905, **38**, 3642—3654. Compare Hantzsch, Abstr., 1900, i, 365).—A mixture of a solution of crystal-violet and hydrochloric acid, when kept at a constant temperature, shows a diminution of electrical conductivity as the time increases until a limiting minimum is reached. This phenomenon indicates a diminution of hydrogen ions due to the formation of a polyacid salt, and ultimately a state of equilibrium between the mono-salt, hydrochloric acid, and the polyacid salt (called by the authors trisalt-β) is attained. This trisalt-β does not appear to be analogous to Hantzsch's trisalt, $C(C_6H_4NMe_2)_3Br(HBr)_2$, which is termed trisalt-α.

The constant K for (mono-salt)$(HCl)^2$/(trisalt-β) is $1 \cdot 12 \times 10^{-3}$.

Hantzsch's trisalt-α on solution in water gives immediately a constant conductivity which is practically identical with the additive value calculated for 1 equivalent of mono-salt + 2 of hydrobromic acid. The conversion into mono-salt is thus practically instantaneous and the constant K for this change can thus not be calculated.

The constants for the incomplete changes: (1) mono-salt + 2HCl $\longrightarrow$ trisalt-β K_1, (2) trisalt-β $\longrightarrow$ mono-salt + 2HCl K_2, have been found to be $K_1 = 5 \cdot 2$ and $K_2 = 5 \cdot 8.10^{-3}$.

The decomposition constant, K_2, for the trisalt-β is not the same as the constant for Hantzsch's carbinol trisalt, ($K_3 = 2 \times 10^{-2}$), and hence the two salts cannot be identical. Full details of the calculations are given. J. J. S.

Action of Hydroxylamine on *apo*Safranones. Otto Fischer and Eduard Hepp (*Ber.*, 1905, **38**, 3435—3438. Compare Abstr., 1903, i, 654; Kehrmann and de Gottrau, this vol., i, 670).—In agreement with Kehrmann and de Gottrau it is found that the compounds obtained by the action of hydroxylamine on *apo*safranone, *iso*rosindone, and ethyl*iso*rosindone are not oximes but the isomeric amino*apo*safranones. Hydroxylamine salts react with *apo*safranone, whereas ammonium chloride is without any influence.

Amino*apo*safranone, prepared by heating *apo*safranone with concentrated alcoholic ammonia under pressure at 140°, is identical with that previously prepared by means of hydroxylamine; both compounds, when heated with sulphuric acid, give the same hydroxy*apo*safranone, proving the amino-group to occupy the ortho-position to the oxygen. E. F. A.

Preparation of *m*-Tolylsemicarbazide. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 160471. Compare this vol., i, 383).—In place of *m*-tolylhydrazine, di-*m*-tolylcarbazide may be allowed to react with carbamide at 160°, yielding *m*-tolylsemicarbazide according to the equation

$$CO(NH{\cdot}NH{\cdot}C_6H_4Me)_2 + CO(NH_2)_2 = 2C_6H_4Me{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2.$$

The same compound is obtained when di-*m*-tolylsemicarbazide is heated with ammonia at 180°. C. H. D.

Azoxonium Compounds. III. FRIEDRICH KEHRMANN (*Ber.*, 1905, **38**, 3604—3607. Compare Abstr., 1901, i, 484; this vol., i, 930).—4 : 8-*Diaminonaphthaphenazoxonium chloride*,

$$\begin{array}{l} \quad C_6H_4{-}C{:}N{-}C{\cdot}CH{:}CH \\ \quad\ | \qquad\ \ | \qquad\ \| \qquad\ \ | \\ NH_2{\cdot}C{:}CH{\cdot}C{:}OCl{\cdot}C{\cdot}CH{:}C{\cdot}NH_2 \end{array},$$

is formed by boiling 2 : 5-diaminophenol hydrochloride with 4-amino-1 : 2-naphthaquinone in alcoholic solution in a reflux apparatus and treating the reaction-product with hydrochloric acid. It crystallises from alcohol in slender, metallic green needles containing water, which is lost at 130°, and is readily soluble in hot water, forming a violet solution with dark red fluorescence, or in alcohol, forming a blue solution with strong red fluorescence; the reddish-brown solution in concentrated sulphuric acid becomes yellow on addition of a small quantity of water, or violet on addition of much water and partial neutralisation of the acid. The aqueous solution dyes tannin-mordanted cotton a bluish-violet, which is fast to soaping and moderately so to light. G. Y.

***endo*Iminotriazoles.** FIRMA EMANUEL MERCK (D.R.-P. 159692).—Triarylated aminoguanidines condense with carboxylic acids or their chlorides to form *endo*iminotriazoles. Thus, triphenylaminoguanidine and concentrated formic acid react at 170—175° to form endo*anilino-diphenyltriazole*,

$$\begin{array}{l} NPh{-}{-}{-}{-}{-}N \\ \ | \qquad\qquad\quad \| \\ CH{<}^{NPh}_{NPh}{>}C \end{array}$$

which crystallises from alcohol in glistening, yellow leaflets, or from chloroform and light petroleum in needles. The salts are highly crystalline, the *nitrate* being insoluble and the *sulphate* and *tartrate* very soluble in water.

endo*Anilinotriphenyltriazole*, from benzoyl chloride and triphenylaminoguanidine, separates from alcohol in glistening, intensely yellow needles and melts at 231—232°. The sparingly soluble *nitrate* melts at 284°; the *hydrochloride* forms flat, colourless needles, melts at 296°, and dissolves readily in water. endo*Anilinodi*-p-*tolyltriazole* separates from chloroform and light petroleum in yellow needles and melts at 167°. C. H. D.

Condensation of Ethyl Succinylsuccinate with Acetamidine. 4 : 9-Dihydroxy-2 : 7-dimethyl-5 : 10-dihydro-1 : 3 : 6 : 8-naphthatetrazine. MARSTON T. BOGERT and ARTHUR W. DOX (*J. Amer. Chem. Soc.*, 1905, **27**, 1302—1305).—It has been shown (this vol., i, 841) that ethyl succinylsuccinate condenses with guani-

dine to form a naphthatetrazine. A similar condensation takes place with acetamidine with production of 4 : 9-*dihydroxy*-2 : 7-*dimethyl*-5 : 10-*dihydro*-1 : 3 : 6 : 8-*naphthatetrazine*,

$$\begin{array}{l} N\cdot C(OH)\!:\!C\cdot CH_2\cdot C\!:\!N\text{——}CMe \\ CMe\cdot N\!=\!C\cdot CH_2\cdot C\!:\!C(OH)\cdot N \end{array},$$

which is obtained as a white powder, and dissolves in ammonia forming a solution with a blue fluorescence, but is insoluble in the usual organic solvents; when heated, it does not melt, but becomes charred. The *sodium* derivative crystallises with $6H_2O$. E. G.

Nitrophenyldiguanides. RICHARD HERMANN (*Monatsh.*, 1905, **26**, 1021—1037).—Nitroanilines do not interact with dicyanodiamide.

p-*Nitrophenyldiguanide* is obtained in the form of its *sulphate*, $(C_8H_{10}O_2N_6)_2,H_2SO_4$, by treating phenyldiguanide hydrochloride with nitric acid of sp. gr. 1·51 and concentrated sulphuric acid at 30—40°. The sulphate crystallises in matted, white, hair-like needles and melts at about 254°. The free base, $C_8H_{10}O_2N_6,H_2O$, separates from alcohol in yellow doubly refractive, prismatic leaflets, loses H_2O at 105°, and melts at 182°. The *picrate* forms a yellow, amorphous precipitate; the *silver nitrate* derivative is obtained as a yellow, flocculent precipitate. When heated with concentrated aqueous potassium hydroxide at 125—130°, the base yields *p*-nitroaniline.

op-*Dinitrophenyldiguanide*, $C_8H_9O_4N_7$, formed by the action of nitric acid of sp. gr. 1·51 and concentrated sulphuric acid on *p*-nitrophenyldiguanide at 75—80°, is obtained in the form of its *sulphate*, $(C_8H_9O_4N_7)_2,H_2SO_4$, which crystallises in yellow needles and melts at 234°. The free base crystallises in doubly refractive, orange-yellow needles, melts at 193°, has a slight basic reaction towards litmus, and yields a yellow, amorphous *precipitate* with silver nitrate. The *oxalate* crystallises in nodular aggregates of broad needles; the *picrate* forms a yellow precipitate. When heated with dilute sulphuric acid at 160—170°, the base is hydrolysed with formation of 2 : 4-dinitroaniline which melts at 181—182° (m. p. 175°; Rudnew, this Journal, 1871, **24**, 712).

2 : 4 : 6-*Trinitrophenyldiguanide sulphate*, $(C_8H_8O_6N_8)_2,H_2SO_4$, formed by the action of nitric acid of sp. gr. 1·51 and concentrated sulphuric acid on *op*-dinitrophenyldiguanide at 105—110°, crystallises in microscopic, broad, yellow leaflets, melts at 270°, and is hydrolytically dissociated when boiled with water or alcohol. The free *base*, $C_8H_8O_6N_8$, crystallises in doubly refractive, microscopic, short leaflets, which appear golden by transmitted, reddish-violet by reflected light, melts at about 239°, and is extremely hygroscopic. When hydrolysed with dilute sulphuric acid, the base yields 2 : 4 : 6-trinitroaniline.

p-*Aminophenyldiguanide sulphate*, $(C_8H_{12}N_6)_2,H_2SO_4$, is formed by electrolytic reduction of *p*-nitrophenyldiguanide in concentrated sulphuric acid and alcohol, with a current density of 3—3·5 amperes and an *E.M.F.* of 1 volt.; it crystallises in broad, white needles and prismatic leaflets, forms with copper sulphate and aqueous alkali hydroxide a rose-red *copper* derivative consisting of fan-shaped aggregates of slender needles, with auric chloride forms a colloidal gold solution, and reduces

ammoniacal silver solutions. When heated with dilute sulphuric acid at 170°, it is hydrolysed with formation of *p*-phenylenediamine.

G. Y.

A New Method of Formation of Diazo-compounds and a General Method for Determining the Constitution of Azo-dyes. OTTO SCHMIDT (*Ber.*, 1905, **38**, 3201—3210).—The action of fuming nitric acid, cooled by ice, on azo-dyes containing an auxochromic amino- or hydroxyl group in the para-position to the azo-group leads to the formation of the diazo-compound from which the dye is prepared, the other component appearing as a nitro-derivative; if the auxochromic group is in the ortho-position, the decomposition takes place completely only with β-naphthol dyes, but partially with *p*-cresol dyes, whilst the reaction takes place only to a small extent or does not take place with azo-dyes containing the auxochromic group in the meta-position. Other azo-compounds, such as azobenzene, are not decomposed by fuming nitric acid.

Azoxy-compounds which contain a *p*-amino-group, such as *pp'*-tetraethyldiaminoazoxybenzene, are decomposed by fuming nitric acid with formation of diazo-compounds. These azoxy-compounds, as also azo-dyes containing an auxochromic group in the para-position, are decomposed in the same manner by chromic or permanganic acids in glacial acetic acid solution.

Helianthin (16·4 grams) yields 8·1 grams of *op*-dinitrodimethylaniline, 1·2 grams of tetranitrodimethylaniline, and diazobenzenesulphonic acid which, when coupled with β-naphthol, forms 19·2 grams of the dye, $OH\cdot C_{10}H_6\cdot N_2\cdot C_6H_4\cdot SO_3Na$, which crystallises in glistening, bronze leaflets. *Tetranitrodimethylaniline*, $C_7H_5O_8N_5$, crystallises from alcohol, is yellow, and melts at 128—129°.

p-*Nitro*-p'-*methoxyazobenzene*, $C_{13}H_{11}O_3N_3$, is formed by the action of methyl iodide and sodium methoxide on *p*-nitro-*p'*-hydroxyazobenzene in boiling methyl-alcoholic solution. It crystallises in yellowish-red, flat needles, melts at 157·5—158°, and when 5 grams are treated with cooled fuming nitric acid yields 2·5 grams of *op*-dinitroanisole melting at 88°, and the diazo-compound, which, with β-naphthol, forms 4·41 grams of *p*-nitrobenzeneazo-β-naphthol, melting at 251·2—252·5°.

When treated with fuming nitric acid, 4 grams of orange II yield 1·7 grams of a *nitro*-derivative of β-naphthol and diazotised sulphanilic acid, which, when coupled with phenol, forms 2 grams of the azo-dye. In the same manner, 2 grams of β-naphtholazobenzene-*o*-carboxylic acid yield 1·4 grams of a nitro-β-naphthol, and 1·8 grams of the dye is recovered by coupling the diazo-compound formed with β-naphthol.

Satisfactory yields of diazo-compounds are obtained from *p*-ethoxy-*p'*-hydroxyazobenzene, *p*-hydroxyazobenzenesulphonic acid, benzene-azo-β-naphthol, and *p*-ethoxybenzeneazo-β-naphthol; but *m*-hydroxyazobenzene, the product obtained on coupling diazotised anthranilic acid with *p*-cresol, azobenzene, *p*-azotoluene, and tetramethyl-*mm'*-diaminoazobenzene, do not yield, or yield only small amounts of, diazo-compounds. [Compare Meldola and Morgan, Trans., 1899, **55**, 608; Meldola and Hanes, *ibid.*, 1894, **65**, 841.]

G. Y.

Stability of Diazotised *p*-Nitroaniline. CARL SCHWALBE (*Zeit. Farb. Text. Ind.*, 1905, **4**, (xviii), 433—456).—The influence of the amount of free hydrochloric acid, free nitrous acid, sodium acetate, or salt on the keeping power of diazotised *p*-nitroaniline has been investigated. The diazo-solutions used were prepared from purified commercial nitrosoamine-red and were titrated against β-naphthol both at the beginning of each experiment and 24 hours later. The experiments show the very harmful influence on the keeping-power exercised by small quantities of nitrous acid, which is still more marked in presence of sodium acetate. Mineral salts are beneficial in increasing the stability when used in conjunction with sodium acetate. Excess of hydrochloric acid also acts beneficially on the keeping-power.

E. F. A.

Properties of *p*-Azophenetole. FRIEDRICH DREYER and TH. ROTARSKI (*Chem. Centr.*, 1905, ii, 1016—1017; from *Isvert. Petersburg. Polytechn. Inst.*, 1905, 135—157).—*p*-Azophenetole, prepared by the reduction of *p*-nitrophenetole with sodium ethoxide, is dimorphous and crystallises from alcohol; it melts and solidifies at 159·35°. The transformation point of the α- into the β-modification is 93·65°. The solubility of the compound in glacial acetic acid is 0·153 gram-molecules per litre at 89·2°, 0·176 at 91°, 0·185 at 93°, 0·209 at 95·6°, 0·232 at 97·2°, and 0·252 at 99·6°; the solubility curve shows a point of inflection at 94·7° corresponding with the temperature of transformation. The α-form crystallises in rhombic plates, has a sp. gr. 1·2314 at 21°/4°, a specific heat 0·350 between 93·7° and 20°, and a coefficient of expansion 0·00033 from 30° to 93·7°, and 0·00078 from 93·7° to 158°. The β-form has a sp. gr. 1·1977 at 21°/4° and a specific heat 0·502 from 93·7° to 159·3°. The molten compound is not doubly refractive and has a specific heat 0·521 from 161·1° to 175·5°. The heat developed by the change of the β- into the α-form is 1·6 and the latent heat of fusion 35·0 calories. E. W. W.

Constitution of the Hydroxyazo-compounds. HERBERT TEICHNER (*Ber.*, 1905, **38**, 3377—3380).—Sodium 1 : 2-naphthaquinone-3 : 6-disulphonate combines with phenylhydrazine sulphate in cold dilute alcoholic solution to form orange-coloured needles,

$$C_{16}H_{10}O_7N_2S_2Na_2,6H_2O;$$

the product is considered to be the *phenylhydrazone*,

$$SO_3Na\cdot C_6H_3{<}\begin{matrix}CO\cdot C{:}N\cdot NHPh\\ \vert \\ CH{:}C\cdot SO_3Na\end{matrix},$$

of the original substance. It is not a derivative of 2-hydroxy-1 : 4-naphthaquinone, as it does not possess tinctorial properties, and, moreover, it is reducible by an excess of phenylhydrazine to 1 : 2-dihydroxynaphthalene-3 : 6-disulphonic acid. It does not condense, moreover, like an ortho-diketone with *o*-tolylenediamine.

The following substances were prepared for comparison. *Sodium 4-anilino-1 : 2-naphthaquinone-3 : 6-disulphonate*,

$$SO_3Na\cdot C_6H_3{<}\begin{matrix}CO\text{———}CO\\ \vert \\ C(NHPh)\cdot C\cdot SO_3Na\end{matrix},4H_2O,$$

is obtained by the action of aniline on sodium 1 : 2-naphthaquinone-

3 : 6-disulphonate ; it forms orange-coloured crystals and condenses with *o*-tolylenediamine, giving a bluish-red, crystalline product, $C_{23}H_{15}O_6N_3S_2Na_2$. Aniline gives with sodium 1 : 2-naphthaquinone-6-sulphonate a product which separates in dark red crystals.

W. A. D.

Aminoazo-dyes from Chlorochromotropic Acid. FARBWERKE VORM. MEISTER, LUCIUS, and BRÜNING (D.R.-P. 160281).—Hypochlorous acid and its salts react with chromotropic acid (1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid) yielding a *chlorochromotropic acid*, in which the chlorine atom probably occupies the ortho-position to one of the hydroxyl groups. This acid does not readily combine with diazotised amines, but combines with diazotised nitroamines, and the resulting compounds may be reduced with sodium sulphide at 50—60° to blue aminoazo-dyes. Thus *p*-nitroaniline, chloro-*p*-nitroaniline, or 2 : 5-nitroaminoquinol dimethyl ether may be employed. C. H. D.

A New Method of Formation of Osotetrazones. WALTER DIECKMANN and LUDWIG PLATZ (*Ber.*, 1905, **38**, 2986—2990. Compare von Pechmann, Abstr., 1898, i, 62).—*a-Chloroglyoxalphenylhydrazone*, COH·CCl:N·NHPh, is formed by the action of phenyldiazonium chloride on chloromalonaldehyde in aqueous sodium acetate solution cooled by ice ; it crystallises from alcohol or benzene in long, yellow needles, melts at 141°, is readily soluble in warm alcohol, ether, glacial acetic acid, benzene, chloroform, light petroleum, or cold acetone, and dissolves in concentrated sulphuric acid, forming a green solution, which becomes red, changing to a dirty-green with ferric chloride, or bluish-violet with potassium dichromate ; when treated with aqueous alkali hydroxides, it decomposes and yields a strong *iso*nitrile odour.

Chloroglyoxalosazone, NHPh·N:CH·CCl:N·NHPh, formed by the action of phenylhydrazine on a-chloroglyoxalphenylhydrazone in alcoholic solution, crystallises in yellow leaflets, melts at 142·5°, is less soluble than the hydrazone, and dissolves in concentrated sulphuric acid, forming a yellow solution which becomes green, changing to blue on addition of potassium dichromate. When treated with alcoholic potassium hydroxide, the osazone is converted into glyoxalosotetrazone, which melts at 152°.

a-Chloro-β-methylglyoxal-a-phenylhydrazone, COMe·CCl:N·NHPh, formed by the action of phenyldiazonium chloride on a-chloroacetylacetone in presence of potassium acetate in aqueous-alcoholic solution, crystallises in yellow needles and melts at 136·5° ; it is moderately soluble in warm alcohol, ether, benzene, chloroform, glacial acetic acid, or cold acetone, and when treated with aqueous alkali hydroxide gives an *iso*nitrile odour. It interacts with phenylhydrazine to form *a-chloro-β-methylglyoxalosazone*, NHPh·N:CMe·CCl:N·NHPh, which crystallises from glacial acetic acid in lemon-yellow leaflets, melts and decomposes at 182·5°, and dissolves in concentrated sulphuric acid to form a yellow solution which becomes bluish-violet on addition of potassium dichromate. When treated with alcoholic

potassium hydroxide, the osazone forms methylglyoxalosotetrazone, melting at 106—107° and decomposing at 124°. G. Y.

The Bence-Jones Proteid. EMIL ABDERHALDEN and OTTO ROSTOCKI (*Zeit. physiol. Chem.*, 1905, **46**, 125—135).—The proteid was obtained from the urine in a case of bone sarcoma. On heating, it is precipitated at 50—60°; this precipitate dissolves on boiling, and reappears on cooling; other properties which are described show it to be similar to the proteid described in previous cases. When a solution of it is injected into rabbits, it does not pass into the urine, and a precipitin is formed in the rabbits' blood, which, however, acts not only on the Bence-Jones proteid, but also on the proteids of normal serum. On hydrolysis, 100 grams yield—glycine, 1·7; alanine, 4·5; leucine, 10·6; proline, 1·9; phenylalanine, 1·5; glutamic acid, 6·0; aspartic acid, 4·5; and tyrosine, 1·7 grams. Lysine, arginine, and histidine were also detected. W. D. H.

The Composition of the Proteid of Aspergillus Niger. EMIL ABDERHALDEN and PETER RONA (*Zeit. physiol. Chem.*, 1905, **46**, 179—186).—*Aspergillus niger* was cultivated on various nitrogenous media; its proteid matter yields on hydrolysis, glycine, alanine, leucine, glutamic and aspartic acids. Aromatic products such as tyrosine and phenylalanine were not discovered. The experiments point to the independence of the proteid and the medium on which the mould is grown, but this cannot be asserted with confidence until quantitative experiments are made. W. D. H.

Influence of Acids and Alkalis on the Swelling of Gelatin. WOLFGANG OSTWALD (*Pflüger's Archiv*, 1905, **108**, 563—589).—The swelling of gelatin in acids and alkalis depends, in a complex manner, on the concentration, the rate increasing with concentration to a maximum at $N/40$ for hydrochloric acid and $N/36$ for potassium hydroxide. With higher concentrations, the rate again diminishes, the fall being at first rapid, then very gradual. Similar results are obtained with other acids and alkalis. The type of curve obtained shows a general parallelism with those representing other properties. The author points out that any theory which attempts to explain the physico-chemical properties of colloids must account for these peculiar curve relations.

The absolute value of the swelling is much larger than in pure water; the absorption of liquid being with acid 3—4 times, and with the optimum alkali 3 times as much. J. J. S.

Formation of Complex Proteids from Peptones. LEOPOLD SPIEGEL (*Ber.*, 1905, **38**, 2696—2702. Compare Henninger, Abstr. 1878, 802, 989; Hofmeister, Abstr., 1879, 950; Loew, Abstr., 1888, 358; Schroetter, Abstr., 1896, i, 515; Blum, Abstr., 1896, i, 658; Lawroff and Salaskin, Abstr., 1903, i, 136; Nürnberg, Abstr., 1904, ii, 187).—When a 5 per cent. solution of commercial peptone is acidified slightly with acetic acid and 1 part of aldehyde in 40 per cent. solution added for each part of peptone, there is formed immediately a

flocculent precipitate which coagulates to a leathery mass; when warmed with dilute sodium hydroxide, this partially dissolves to form a solution which on acidification with acetic acid and warming deposits a small coagulate on the walls of the glass vessel.

The precipitate obtained from a peptone of unknown genesis contained C = 48·78, H = 7·39, N = 16·63, S = 1·29, and ash = 0·023 per cent., whilst that from a specimen of Witte's peptone contained C = 49·55, 50·31, H = 8·63, 7·55, N = 13·75, S = 1·11, and ash = 0·165 per cent. The filtrate from the flocculent precipitate becomes opaque on warming, and this precipitation is greatly increased on adding acetic acid, whereas a solution of peptone slightly acidified with acetic acid remains clear when heated by itself, or with a further addition of acetic acid, or in presence of 1 per cent. of sodium chloride. The filtrate gives positive results with the xanthoprotein, Spiegler's, the biuret, and Adamkiewicz's reactions for albumin, as also with concentrated nitric and sulphuric acids, and with concentrated sulphuric acid and saccharose; it blackens alkaline lead solutions on boiling. An acidified solution of peptone gives a yellowish-brown coloration with the xanthoprotein and only a slow precipitation with Spiegler's reagent.

Fractional precipitation experiments according to Pick's method (Abstr., 1898, i, 288) show that in the formaldehyde-peptone filtrate the albuminoses which are soluble in semi-saturated ammonium sulphate solution have been converted into albumins, which are easily salted out, and part of which correspond with Fuld and Spiro's euglobulin (Abstr., 1901, ii, 67).

Pure peptone is obtained by saturating an aqueous solution of Witte's peptone with ammonium sulphate, concentrating the filtrate, and precipitating the ammonium sulphate with alcohol. This, when treated with formaldehyde in aqueous solution at the winter temperature, remains clear even if saturated immediately with ammonium sulphate, but forms a precipitate if saturated after some days, and after two months becomes opaque when warmed with 1 per cent. of sodium chloride. If the treatment with formaldehyde is carried out at the summer temperature, condensation takes place immediately, with formation of a precipitate which dissolves in dilute sodium hydroxide to form a solution from which acids precipitate a substance with the properties of an alkali albuminate. The filtrate from the condensation precipitate forms a precipitate when half saturated, and again when completely saturated with ammonium sulphate.

When distilled, the alkaline solution of the condensation precipitate yields a distillate which has an odour resembling that of formaldehyde and precipitates a black powder from warm ammoniacal silver nitrate solution, but does not give the formaldehyde reaction with alkaline resorcinol. The residual alkaline liquid does not form a precipitate when acidified. The condensation precipitate does not yield formaldehyde when heated with acids. G. Y.

Adrenaline [Epinephrine], the Active Principle of the Suprarenal Glands. THOMAS B. ALDRICH (*J. Amer. Chem. Soc.*, 1905, **27**, 1074—1091).—A *résumé* is given of the work on adrenaline

together with a discussion of its constitution. The author quotes analyses in support of the formula $C_9H_{13}O_3N$, which he was the first to ascribe to the compound (Abstr., 1901, ii, 564). A bibliography of the subject is appended. E. G.

Behaviour of Ferments towards Colloidal Solutions. EMIL REISS (*Beitr. chem. Physiol. Path.*, 1905, **7**, 151—152. Compare Dauwe, this vol., i, 623).—When chloroform solutions of lecithin are shaken with solutions of ferments, it is found that part of the ferment is transferred to the chloroform solution. This holds good for rennin and trypsin. The catalase of milk adheres to the milk globules, but if these are separated from the plasma and covered with water or sodium chloride solution, the catalase is dissolved by these liquids, indicating that the enzyme is precipitated by the colloidal plasma, but in the absence of such colloids is readily soluble. J. J. S.

Catalase. PHILIP SHAFFER (*Amer. J. Physiol.*, 1905, **14**, 299—312).—The main conclusion drawn from the experiments recorded is that the catalase action of plant and animal extracts liberates oxygen in a molecular condition. It is therefore not an oxidising enzyme, but destroys the peroxide in such a way that oxygen is not liberated in an active condition ; the tissues are thus protected from injurious oxidation. W. D. H.

Is the Presence of a Catalase necessary for the Guaiacum Reaction? LEO LIEBERMANN and PAUL LIEBERMANN (*Pflüger's Archiv*, 1905, **108**, 489—498. Compare *ibid.*, 1903, **104**, 207).—Heating malt-extract above 80°, or shaking it with mercuric oxide and magnesia, destroys the catalase which causes the decomposition of hydrogen peroxide, but the solution still induces the guaiacum reaction, particularly if oil of turpentine is present. Hence the authors conclude that, contrary to the view held by Neumann-Wender (*Enzymologishe Studien*, I, 28—35, Berlin, 1904), only one enzyme, the oxygen-carrier peroxydase, is necessary for inducing the reaction. J. J. S.

Precipitins. IVAR BANG (*Beitr. chem. Physiol. Path.*, 1905, **7**, 149—150).—As regards limits of precipitation of precipitin, it is found in the same fraction as euglobulin, and after dialysis remains in the soluble portion and may be precipitated by sodium chloride. When the dialysed solution is heated, albumin coagulates at 64° and precipitin is contained in the filtrate.

Precipitins obtained by injecting ox-blood-serum into dogs do not always behave in the same manner ; some give precipitates with both globulin and serum-albumin, others with globulin only. J. J. S.